

YATSIMIRSKII, K. B.

PA 18T91

USSR/Chemistry - Entropy
Chemistry - Ions

May 1947

"The Standard Entropies of Ions in the Crystalline State," K. B. Yatsimirskii, Chemical-Technological Institute, Ivanovo, 2 pp

"Zhur Fiz Khim" Vol XXI, No 5

Lists the values as discovered by E. N. Gapon and the different values derived by later experimentation.
Published 17 Dec 1946.

18T91

YATSIMIRSKIY, K. B.

USSR/Chemistry - Ions
Chemistry - Cations

Dec 1947

"Thermochemical Radii of Ions in Solution," K. B. Yatimirskiy, 4 pp

"Dokl. Akad. Nauk SSSR, Nova Ser" Vol LVIII, No 7

Uses method of calculating radii of ions from thermochemical data to calculate this data for several ion solutions. Method consists of finding magnitude of energy of a lattice from thermochemical and spectroscopic data, according to the equation

$$U = -\Delta H_k - \Delta H_x - \Delta H_{kx},$$

where U is the energy of the lattice,
 $-\Delta H_k, -\Delta H_x$ are the energy of the lattice,
 $-\Delta H_{kx}$ is the energy of the lattice.

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USSR/Chemistry - Ions (Contd)

Dec 1947

and $-\Delta H_{kx}$ are the heat of formation of a gaseous cation, a gaseous anion, and hard salt. Submitted by Academician I. I. Chernyayev, 18 Jun 1947.

60710

186 AND 6TH (CDS1)

PROCEDURES AND PROPERTIES NOTES

2

The hexachlorostannate series. K. B. Vatskiretski (N. S. Kurnakov Inst. Gen. Inorg. Chem. Acad. Sci. U.S.S.R., Moscow). *Invent. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* 1948, 263-8; cf. *ibid.* 1949, 461. The heat of the reaction $\text{SnCl}_4 + 2\text{Cl}^- \rightarrow \text{SnCl}_6^{2-}$, in the gaseous state, is taken = 17.3 kcal./mole, and the radius of the SnCl_6^{2-} anion = 2.98 Å. (from the K_2SnCl_6 lattice). Then by Kapustinskii's equation for the lattice energy (C.A. 34, 6705) the heat of formation Q of the complex salt from the simple salt and the addend = $[287.3 + 2(n + m)Z_1/(r_1 + 3.98)] [1 - [0.345/(r_1 + 3.98)]] - [287.32 (Z_1 + 1)/(r_1 + 1.81)] [1 - [0.345/(r_1 + 1.81)]] - 17.3]$, where r_1 = radius of the cation, 1.81 = radius of Cl^- , Z_1 = charge of the cation, n = no. of cations, m = no. of SnCl_6^{2-} anions in the mol. Numerical solution of this equation gives the conditions of stability of hexachlorostannates, namely, for salts of the type $\text{M}^{\text{II}}(\text{SnCl}_6)_x$, $Q > 0$ if $r_2 > 0.4$ Å., for salts of the type $\text{M}^{\text{III}}(\text{SnCl}_6)_x$, $Q > 0$ if $r_2 > 1.5$ Å., and for salts of the type $\text{M}^{\text{IV}}(\text{SnCl}_6)_x$, $Q > 0$ if $r_2 > 3.7$ Å. It accounts satisfactorily for the fact that, although chlorostannates of $[\text{M}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ aquo cations are stable, those of the anhyd. simple cations M^{II} are not, as the latter do not attain the crit. size of 1.5 Å. There are no chlorostannates of Ba^{2+} or Pb^{2+} , as these cations form no stable aquo ions. It further becomes evident why chlorostannates of big cations such as $[\text{M}(\text{CO}_2\text{N}_2\text{H}_2)_6]^{2+}$ are stable. The following chlorostannates were prepd.: By mixing the stoichiometric amts. of FeCl_3 , $\text{Co}(\text{NH}_3)_6$, and SnCl_4 and evap. on a water bath to beginning crystals, one obtains $[\text{Fe}(\text{CON}_2\text{H}_2)_6](\text{Cl})(\text{SnCl}_6) \cdot 15\text{H}_2\text{O}$, readily sol. in H_2O , stable in air, losing H_2O at $70-80^\circ$; with excess SnCl_4 , one gets the yellowish $[\text{Fe}(\text{CON}_2\text{H}_2)_6](\text{SnCl}_6) \cdot 15\text{H}_2\text{O}$. On mixing concd. solns. of $[\text{Cr}(\text{CON}_2\text{H}_2)_6]\text{Cl}_3$ and SnCl_4 , one obtains a ppt. of light-green crystals $[\text{Cr}(\text{CON}_2\text{H}_2)_6](\text{Cl})(\text{SnCl}_6)$, stable in air, losing H_2O at $90-100^\circ$. When the calcd. amts. of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and of $\text{Co}(\text{NH}_3)_6$ are dissolved in a 60% aq. soln. of SnCl_4 , and the soln. is heated 10-20 min. on a water bath and left in a desiccator over H_2SO_4 for 5-6 days, the salt $[\text{Ca}(\text{CON}_2\text{H}_2)_6](\text{SnCl}_6)$ is pptd. $[\text{Mg}(\text{CON}_2\text{H}_2)_6](\text{SnCl}_6)$ is obtained in an analogous way. N. Thon

COMMON ELEMENTS

COMMON VARIABLES MORE

ASS-5LA METALLURGICAL LITERATURE CLASSIFICATION

820000 SYNTHESE

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YATSIMIRSKIY, K.B.

Yatsemirskiy, K.B. and Zaslavskiy, I.I. "Classification of diagrams in volumetric analysis of liquid double systems," (reference), Soobshch. o nauch. rabotakh chlenov Vsesoyuz. khim. o-va im. Mendleyeva, 1948, Issue 2, p. 23

SO: U-2888, Letopis Zhurnal'nykh Statey, No. 1, 1949

YATSIMIRSKIY, K. B.

8/49T13

USSR/Chemistry - Heat of Hydration, Of Ions Jul/Aug 48
Chemistry - Thermochemistry

"Thermochemical Radii and Heats of Hydration of Ions,"
K. B. Yatsimirskiy, Inst Gen and Inorg Chem Imeni N. S.
Kurakov, Acad Sci USSR, 7 1/2 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4

Calculates thermochemical radii and heats of formation
in the gaseous state of the ions: JO_3^- , BrO_3^- , CNO^- ;
 $\text{C}_6\text{H}_5(\text{NO}_2)_3\text{O}^-$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+$.
Calculates heats of hydration of the ions:
 ClO_4^- , $\text{C}_6\text{H}_5(\text{NO}_2)_3\text{O}^-$, ClO_3^- , BrO_3^- , NO_3^- , HCO_3^- , CNO^- ,
 H_2COO^- , KCO_3^- , CNS^- , CN^- , $[\text{N}(\text{CH}_3)_4]^+$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+$.
Shows relation between heat of hydration and magnitude
8/49T13

USSR/Chemistry - Heat of Hydration, Of Ions Jul/Aug 48
(Contd)

of thermochemical radius. This relation for anions of
the type RO_n^- is somewhat different from that for other
anions. Shows applicability of Kapustinskii's
equation for calculating the entropies of RO_n^- type
ions in aqueous solution. Presents heat
of solution of salts as a function of the ion radii
which form the particular salt. Establishes general
relationship between alteration of heat of solution and
the magnitude of the ion radii. Submitted 11 Jun 1947.

8/49T13

YATSMIRSKIY, K. B.

PA 27/49T32

USSR/Chemistry - Lanthanum Compounds Sep/Oct 48
Chemistry - Ionization, Potential of

"Calculation of the Potentials of Ionization for
Some Lanthanides by Means of Kapustinskiy's
Equation," K. B. Yatsmirskiy, Inst Gen and Inorg
Chem imeni N. S. Kurnakov, Acad Sci UFSR, Ivanovo
Chem Eng Inst, 2 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 5

Found a regular increase in the ionization potential
of the lanthanide series, Ce-37.1 ev, Pr-37.7 ev,
Nd-38.2 ev, Sm-38.2 ev, and Er-40.0 ev. Submitted
5 Apr 48.

27/49T32

PA 33/49T20

YATSIMIRSKIY, K. B.

USSR/Chemistry - Synthesis
Chemistry - Energy, Lattice, of Metal Salts
Nov/Dec 48

"The Lattice Energy of Metal Salts of Secondary
Groups in a Periodic System," K. B. Yatsimirskiy,
Inst Gen and Inorg Chem imeni N. S. Kurnakov,
Acad Sci USSR, 11 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 6

Studies condensation of 2-formoxybutadiene, 2-
methoxybutadiene, and chloroprene with divinylke-
tones (5-methyl-1,4-hexadiene-3-onium and 5-
methyl-1,4-octadiene-3-onium). Shows that re-
action takes place easily according to General

33/49T20

USSR/Chemistry - Synthesis (Contd.) Nov/Dec 48

diagram of diene synthesis with formation of
corresponding pair-substituted derivatives of
cyclohexenylketones. Submitted 10 Nov 47.

33/49T20

YATSIMIRSKIY, K. B.

PA 67/49T40

USSR/Chemistry - Salts, Ammine
Cobalt

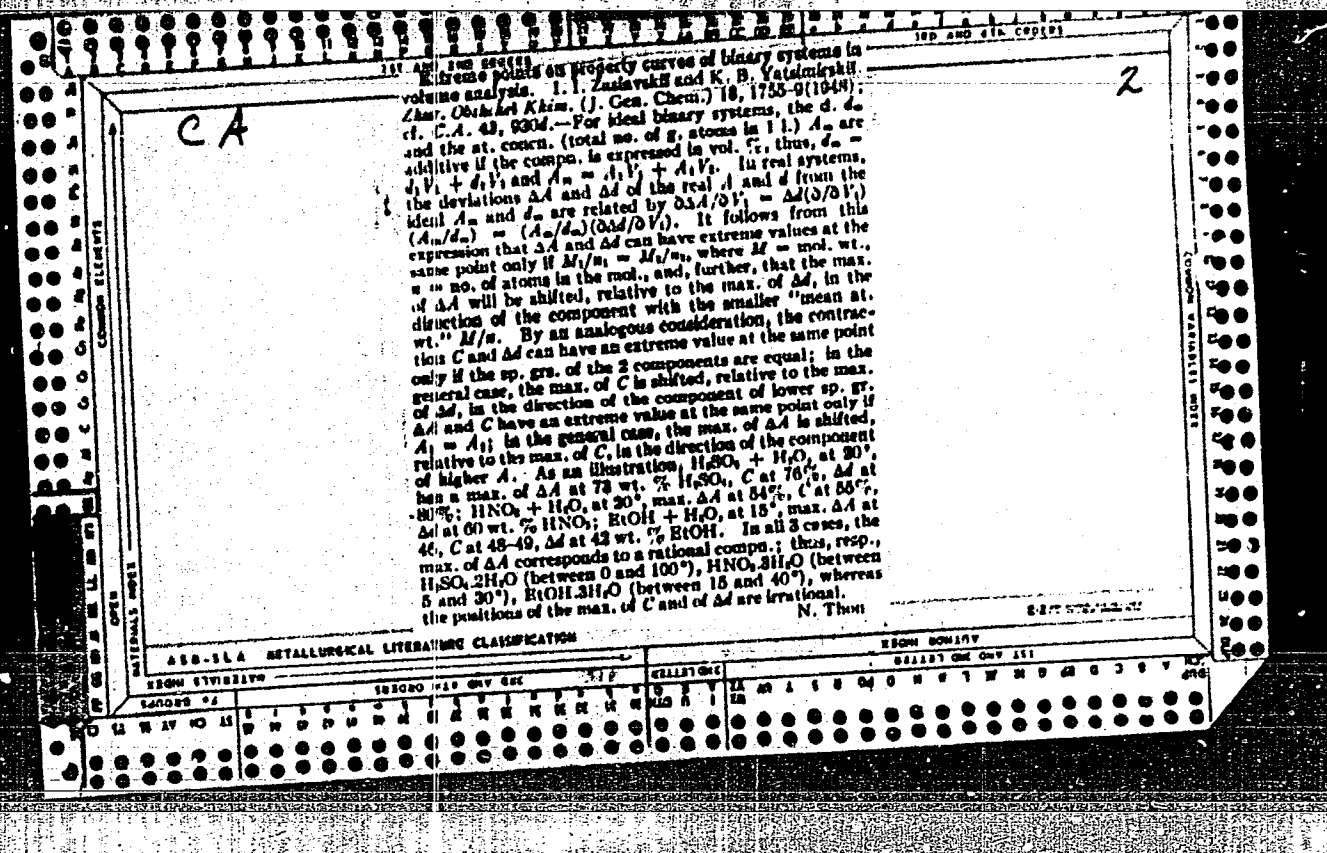
Dec 48

"Thermochemistry of Cobalt Acidopentamine Salts,"
K. B. Yatsimirskiy, L. L. Pankova, Chair of
Inorg Chem, Ivanovo Chemicotechnol Inst, 7 $\frac{1}{2}$ pp

"Zhur Obshch Khim" Vol XVIII, No 12

Determined heats of formation and heats of
solution for a large number of salts such as
(Co(NH₃)₅Cl)Br₂, (Co(NH₃)₅SO₄)I, etc. Made a
study of the thermochemistry of their ions.

67/49T40



26

B

ENTROPIES OF IONS IN CRYSTALS AND SOLUBILITY OF SALT.
(In Russian.) A. F. Kapustinakii and K. B. Yatsi-
mirskii, *Zhurnal Fizicheskoi Khimii* (Journal of
Physical Chemistry), v. 22, Oct. 1948, p. 1271-1279.
Presents results of experimental and theoretical
study. Data are tabulated and charted. 16 ref.

ASA-SLA METALLURGICAL LITERATURE CLASSIFICATION

62 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99

100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200

IATSIMIRSKII, K. B.

I. I. Zaslovskii and K. B. Iatsimirskii, Unusual points on the curves of properties of binary systems during volumetric analysis. p. 1755

Mathematical analysis has established the following for 2-compound systems by chemical reaction: The maximum deviation of atomic concentration from the average of calculated value (ΔA) is shifted in regards to the maximum deviation of specific gravity from the average calculated value (Δd) toward the component with the smaller average atomic weight. The maximum ΔA is shifted in regard to the compression maximum C toward the component with the largest atomic concentration. The maximum Δd is shifted in regards to the maximum C toward the component with the largest specific gravity.

✓ Chair of Inorganic Chemistry of the Ivanov Chemical Technological Institute
July 17, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 10 (1948):

¹⁵
YAKIMIRSKIY, K. B.,

K. B. Yakimirskii and L. L. Pankova, Thermo-chemistry of acido-pentaammine salts of cobalt. p. 2051.

The heat of reaction is determined with a 0.26 in solution of Na_2S and from this is calculated the heat of formation of 15 compounds and the heat of solution of 13 compounds. The heat of formation is calculated for a series of complex acido-penta-ammine cobalt-ions in a water solution. From this is calculated the heat of formation of certain salts.

Chair of Inorganic Chemistry of the
Ivanov Chemico-Technological
Institute
June 28, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 12, (1948)

YATSIMIRSKIY, K.B.

29573

Ie istorii analitichyeskoy khimii v rossii. Uspyekhi Khimii,
1949, vyp.5, s.623-28. Bibliogr: s.628

4. Gyeologo-Gyeorafichyeskiye Nauki
(Palyeontologiya - Sm. XV, 5 B)

a. Gyeologo-Gyeografichyeskiye Nauki b Tsyelom. Gyeologiya. Pyetrografiya.
Minyeralogiya. Kristallografiya.

SO: LETOPIS' NO. 40

1ST AND 2ND COLUMNS										3RD AND 4TH COLUMNS									
PROCESSES AND PROPERTIES INDEX																			
<p>3014 The Energetics of the Lanthanide Ions. K. B. Yatsimirskii. Invest. Akad. Nauk S.S.S.R., Otd. Khim. Nauk, No. 6, 648-511(1949)(in Russian).</p> <p>Thermochemical characteristics of rare earths, such as ionization potentials, and hydration and formation heats, of their trivalent ions, were determined by using the equation of Kapustin'skiĭ (Zhur. Obshchei Khim. 13, 497(1943)) and the known thermochemical data. Thus, the formation heats $-H_R$ of the gaseous ions La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Lu^{3+} were found from $-H_R = 3H_{Cl} - U_{Cl}$, $-H_{Ac}$, where H_{Cl} and $-H_{Ac}$ are formation heats of the gaseous Cl^- and the solid salt, respectively, and U_{Cl} is the energy of the latter's lattice, calculated from Kapustin'skiĭ's equation. Since the formation heat of a gaseous ion is the sum of the metal's sublimation and ionization heats, and since the ionization heat is approximately equal to the ionization potential I, the latter can be calculated, by using the value 90 kcal for the sublimation heat of the lanthanides. The values found satisfy the equation $I = 49.18 \log Z - 38.9$, from which the ionization potential of the element 61, Eu^{3+}, Tb^{3+}, and Yb^{3+}, can be calculated. Further, the hydration heats $L_R = -H_{aq} + H_R - 3 \times 101$, where 101 kcal is the heat of formation of a H ion in water solution, and the difference $H_{aq} - 303$ is the heat of formation of a trivalent lanthanide ion in water solution. The values thus calculated satisfy the equation $L_R = 382 + 519/r$, where r is the ion radius. By using the material obtained in the present work, an estimation can be made of the heats of formation of various compounds, such as chlorides, hydroxides, oxides, nitrates, sulfates, etc., of the lanthanides.</p>																			
<p>ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION</p>																			
FROM SYNONYMS										FROM DEFINITION									
SYNONYMS										DEFINITION									

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Diagrams of the type ionic radii-property. K. B. Yatsimskii (Ivanovo Chem.-Technol. Inst., Ivanovo, U.S.S.R.). *Izvest. Sektora Fiz.-Khim. Anal. Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R.* No. 19, 203-10 (1949).
 —For this type of diagram where the properties are lattice energy, heat of soln., and soly. cf. C.A. 42, 4870c, 4870d, and 48, 1941f. Analogous diagrams were constructed for ionic radii vs. \log ρ . The diagram ionic radii-crystal structure differed from the preceding ones. When values of r_+ were plotted as abscissa and r_- as ordinate, where c and a designate cation and anion, resp., and when line AB was drawn for $r_+/r_- > 0.87$ and line CD for $r_+/r_- = 0.41$, it could be expected, according to Magnus and to Goldschmidt, that to the right of AB the crystal structure would be that of CaCl_2 , yet out of 19 salts 3 crystals, as expected, 9 were of the NaCl type, and 7 had both structures. Similarly, between AB and CD the NaCl type of structure was expected, yet NH_4I having both types of structure was located there. The diagram showed that the CaCl_2 structure appeared where $r_+ > 1.6$ A. and $r_- > 1.9$ A. Both CaCl_2 and NaCl types occurred where $r_+ > 1.35$ A. and $r_- > 1.7$ A. Thus, the type of crystal structure depended on the absolute value of r .
 M. Haseh

CA

Thermochemistry of complex cobaltic salts with neutral
additives. K. D. Yatsimirskii and I. L. Pankova (Ivan-
ovo Inst. Chem. Technol.). *J. Gen. Chem. U.S.S.R.*
10, 800-75(1949) (English translation).—See *C.A.* 43,
7415g. R. J. C.

C4

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Thermochemical relations in the Werner-Mischel
series for complex cobaltic compounds. K. B. Yashin,
and L. L. Pashova (Ivanovo Inst. Chem. Technol.),
J. Gen. Chem. U.S.S.R. 19, 677-68 (1966) (English trans-
lation).—(see C.A. 48, 7806d.
E. J. C.

Thermochemical radii and energies of tetrahedral and triangular ions. A. F. Kapustin and K. B. Yatsimirskii (Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshch. Khim.* (J. Gen. Chem.) 19, 2191-2200 (1949). — (1) Thermochem. radii r calcd. for a given anion by K. 's equation (C.A. 23, 3709) from the lattice energy U , show very slight variations, of the order of 3%, depending on the nature of the cation of the salt, in the sense that r of the nonspherical anion increases when it is assoc. with a larger cation;

e.g., NO_3^- , r varies from 1.86 in CaNO_3 to 1.94 Å. in $[\text{Co}(\text{NH}_3)_4]\text{Cl}(\text{NO}_3)$; ClO_4^- , from 1.98 in RbClO_4 to 2.05 Å. in $[\text{Ni}(\text{H}_2\text{O})_6]\text{ClO}_4$; HCO_3^- , from 1.56 in $[\text{Zn}(\text{NH}_3)_6](\text{HCO}_3)_2$ to 1.60 in $[\text{Co}(\text{NH}_3)_6](\text{HCO}_3)_2$; SO_4^{--} , from 2.33 in CaSO_4 to 2.33 in $[\text{Co}(\text{NH}_3)_6]\text{ClSO}_4$; CrO_4^{--} , from 2.37 in $[\text{Co}(\text{NH}_3)_6]\text{BrCrO}_4$ to 2.42 in $[\text{Co}(\text{NH}_3)_6]\text{NO}_3\text{CrO}_4$; O_3^{--} , 1.79 in BaO_3 , 1.80 in CaO_3 and SrO_3 . A smaller cation penetrates more deeply into recesses of the anion and thus brings about a decrease of its r . (2) In heats of hydration Q of anhyd. salts, calcd. by $Q = U_0 - U + W$, where U_0 = lattice energy of the hydrated salt, the heat of formation W of the gaseous aquo ion from the gaseous central ion and gaseous H_2O remains const. in the case of salts of spherical anions (F^- , Cl^- , Br^- , I^-) but anomalies appear with nonspherical anions; thus, instead of increasing with the size of the anion, Q is greater for chlorides than for nitrates, and the same reversal

is found between bromides and chlorates. This reversal is due to a decrease of the "penetration effect," present in the case of polyanions, as a result of the hydration of the cation. Illustrative data of Q , in kcal./mole, are: $[\text{Li}(\text{H}_2\text{O})_4]\text{Cl}$ 42.3, $[\text{Li}(\text{H}_2\text{O})_4]\text{NO}_3$ 40.0, $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}$ 36.9, $[\text{Mg}(\text{H}_2\text{O})_6]\text{NO}_3$ 28.8, $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}$ 36.3, $[\text{Ca}(\text{H}_2\text{O})_8]\text{Cl}$ 11.8, $[\text{Ca}(\text{H}_2\text{O})_8]\text{NO}_3$ 14.0, $[\text{Ca}(\text{H}_2\text{O})_8]\text{Cl}$ 89.4, $[\text{Ca}(\text{H}_2\text{O})_8]\text{NO}_3$ 84.4, $[\text{Ba}(\text{H}_2\text{O})_{10}]\text{Cl}$ 16.6, $[\text{Ba}(\text{H}_2\text{O})_{10}]\text{NO}_3$ 14.4, $[\text{Ba}(\text{H}_2\text{O})_{10}]\text{Cl}$ 15.3, $[\text{Ba}(\text{H}_2\text{O})_{10}]\text{NO}_3$ 12.7. (3) The value of r lies somewhere between the min. distance of max. penetration and the radius of the circumscribed sphere. The distance d between the central atom of the complex anion and the cation is not equal to the sum of the thermochem. radii r calcd. for an octahedral surrounding, but, for a given lattice type, the ratio of d and the sum of r is a const.; thus, for the barite type (BaSO_4 , BaSO_3 , PbSO_4), that ratio = 1.05, and for the calcite type (CaCO_3 , MnCO_3 , NaNO_3), 0.90. For a given type of anion, the ratio of r and the radius of the circumscribed sphere is a const., thus, for triangular ions (NO_3^- , CO_3^{--}) it is = 0.67; for tetrahedral ions (ClO_4^- , MnO_4^- , BF_4^- , SO_4^{--} , CrO_4^{--} , MoO_4^{--}) it varies between 0.76 and 0.81, mean 0.79 = 0.03. This relation permits calcu.

of r for anions for which the radius of the circumscribed sphere is known; thus, for BO_3^{--} , r (calcd.) = 1.91, BeF_4^{--} 2.45, IO_4^{--} 2.49, SeO_4^{--} 2.43, TeO_4^{--} 2.54, PO_4^{--} 2.36, AsO_4^{--} 2.48, SbO_4^{--} 2.60, BiO_4^{--} 2.66 Å. (4) In groups of the periodic system, the r of anions of analogous structure increase regularly with increasing at. no. of the elements. (5) Heats of formation of the gaseous anion are calcd. by $-\Delta H_A = \Delta H_C - \Delta H_{CA} - U_{CA}$, where the subscripts A , C , and CA refer to the gaseous anion, the gaseous cation, and the solid salt, resp., and the ΔH 's are calcd. from the ionization potentials and the heats of sublimation of the metals; for TeO_4^{--} and SbO_4^{--} , the ΔH 's were calcd. from the heats of formation of the ions in soln. and their heats of hydration Q . Values of r , ΔH_A , and Q , are: NO_3^- 1.89, 80.8, 70.7; ClO_4^- 2.00, 87.4, 64; ClO_3^- 2.36, 91.5, 50; MnO_4^- 2.40, 174, 49; IO_3^- 2.46, 96, (40); CO_3^{--} 1.85, 47, 317; CrO_4^{--} 2.4, 182, 229; SO_4^{--} 2.3, 178, 241; SeO_4^{--} 2.43, 124, 224; MoO_4^{--} 2.51, 230, 216; TeO_4^{--} 2.54, 155, (216); WO_4^{--} 2.57, 266, 203; BO_3^{--} 1.91, -240, 190; PO_4^{--} 2.38, 50, 590; AsO_4^{--} 2.48, -20, 590; SbO_4^{--} 2.60, -20, (513); BiO_4^{--} 2.6, (-380), --. (6) The calcd. values of $-\Delta H_A$ permit a decision between the Kossel scheme representing the structure of the BO_3^{--} ion by ionic bonds between a cen-

tral B^{++} ion and 4 O^{--} ions, and the Lewis scheme involving covalent bonds between B^{++} and 4 O^- . The energy of the process $\text{B}^{++} + 4 \text{O}^{--} = \text{BO}_3^{--}$ is calcd. to be 4000 kcal., that of $\text{B}^{++} + 4 \text{O}^- = \text{BO}_3^{--}$ to be 725, as against 7340 and 1000 kcal., resp., from the ΔH_A data. Consequently, the Lewis structure is distinctly predominating. The same holds for the anions ClO_4^- , PO_4^{--} , SiO_4^{--} , AsO_4^{--} , SbO_4^{--} , NO_3^- , CO_3^{--} , BO_3^{--} , ClO_3^- , all of which prove to be predominantly built of singly charged O^- ions covalently bonded with the central ion. The Kossel structures become somewhat more probable as the degree of oxidation of the central ion decreases, but their share never becomes significant. (7) Exptl. detn. of the heat of soln. of NaIO_4 in H_2O at 25° gave -8910 cal.; with the

heat of formation of NaIO_4 in aq. soln. = 95.1 kcal.; this gives for solid NaIO_4 , $\Delta H_{\text{soln}} = -104.0$ kcal.

N. Thon

2

Thermodynamics of aqueous salts of manganese. K. B. Valentinov and A. A. Astasheva (Ivanovskii Khim.-Tekhn. Inst.). Doklady Akad. Nauk S.S.S.R. 69, 381-3 (1949); cf. ibid. 30, 1407 (1947); C.A. 43, 2168d. Owing to the difficulty of prep. $[\text{Mn}(\text{H}_2\text{O})_6]\text{Cl}_2$ with exactly 4 H_2O , the heat of soln. in H_2O , at 25 = 0.08°, is reported as a means of 11 deter. made on preps. with 4.3, 4.08, 4.08, 3.98, and 3.7 H_2O ; the av. value inter-
 pointed to 4 H_2O is 8680 cal., different from the figure of Thomson and of Farver (C.A. 20, 8829°). This gives for the heat of formation $\Delta H_{\text{f}}^\circ = -398.7$ kcal. Further deter. of heats of soln. gave: $[\text{Mn}(\text{H}_2\text{O})_6]\text{Br}$, 4020 cal., $\Delta H_{\text{f}}^\circ = -376.1$ kcal.; $[\text{Mn}(\text{H}_2\text{O})_6]\text{I}$, 3480 cal., $\Delta H_{\text{f}}^\circ = -341.0$ kcal.; $[\text{Mn}(\text{H}_2\text{O})_6]\text{Br}$, at 9° (because of the decomposition above 13°), -408 cal., $\Delta H_{\text{f}}^\circ = -317.3$ kcal. With the previously detd. heat of soln. of 6 H_2O (gas) to Mn^{2+} (gas), -268 kcal., and Mn^{2+} (gas) + 4 H_2O (gas) = $[\text{Mn}(\text{H}_2\text{O})_4]^{2+}$ (gas) - 188 kcal., based on the calcns. of Kley and Evans (C.A. 32, 8897°), the heat of formation of the gaseous ion $[\text{Mn}(\text{H}_2\text{O})_4]^{2+}$ is $\Delta H_{\text{f}}^\circ = 177$ kcal. Hence, by the energy difference of the solid salt and the gaseous ions, the lattice energy of solid $[\text{Mn}(\text{H}_2\text{O})_6]\text{Cl}_2$ is 480.7 kcal., and, by the equation of Kapustinikh (C.A. 33, 5708°), the thermodynamic radius of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is 1.63 Å. The calcd. $\Delta H_{\text{f}}^\circ$ values are in very good agreement with the exptl. values, but differ, by 11.4-13.7 kcal., from the figures of Bichowsky and Rossini, which are based on old erroneous data of Leacock (Ann. chim. phys. 28, 423 (1843)).
 N. Thou

CA

2

Classification of diagrams in volume analysis of liquid binary systems. K. B. Yatsimirskii and I. I. Zaslavskii (Ivanovo Chem. Technol. Inst.) *Zh. Obshch. Khim.* (J. Gen. Chem.) 20, 201 (1950).-- Diagrams of the at. concn. A as a function of the compn. are of 4 types: In ideal systems of noninteracting liquids of unchanging degree of assocn., A is a linear function of the compn., and the deviation ΔA from additivity is zero throughout. In systems with one assoc. component which, in soln., dissociates into simpler units, the curve of ΔA is convex to the axis of compn., and ΔA is always neg. In systems where the components form chem. compds., ΔA is concave to the axis of the compn. In systems involving both compd. formation and dissociation of one or both assoc. components, the ΔA curve is slightly concave to the axis of abscissas; the abs. values of ΔA are relatively low, and the max. of ΔA may not correspond to the compn. of the compd. Examples of ideal systems are EtOH-AcOH, CCl₄-CCl₂, CCl₄-PhBr, AcOMe-HCO₂Et, CCl₄-PhCl, CCl₄-PhMe, CCl₄-PhMe, CCl₄-C₆H₅Br, CCl₄-C₆H₅Br, etc.; for all these systems, plots of ΔA and of the sp. gr. against the compn. in mole fractions are linear, although the viscosity isotherms may show a min. or a max. Linear plots of ΔA may be found also with systems of assoc. but chemically close substances, as MeOH-PrOH and HCO₂H-AcOH. Very slight deviations from additivity, with consistently neg. ΔA , are exhibited by CCl₄-CS₂, PhMe-CS₂, CHCl₃-CS₂, C₆H₅Br-CS₂, C₆H₅Br-CS₂, CCl₄-CHCl₃, C₆H₅-Et₂O, C₆H₅-C₆H₅Br, etc.; very small pos. ΔA is found in C₆H₅Br-CHCl₃ and CS₂-PhBr. The 2nd type, with dis-

tinctly neg. ΔA , is exemplified by CCl₄-AcOH, CCl₄-Me₂CO, CS₂-Me₂CO, EtBr-AcOH, PhMe-AcOH, CCl₄-PrOH, MeI-Me₂CO, CS₂-PrOH, etc.; viscosity isotherms of some of these systems may have either a min. or a max., and are, consequently, less informative than the ΔA plots. In the 3rd type, the ΔA curve consists of 2 branches intersecting at the max.; depending on whether, along a branch, A and ΔA are syzygetic, antibatic, or const., the branch is convex to the axis of compn., concave to it, or rectilinear. One single compd. is indicated by a singular point, whereas in the case of presence of several compds., the max. is rounded, as in HClO₄-H₂O, HNO₃-H₂O, HF-H₂O, H₂SO₄-H₂O, H₃PO₄-H₂O, N₂H₄-H₂O, H₂SO₄-Et₂O, etc. "Irrational" systems of the 4th type, showing a flat diffuse max., are illustrated by PhOH-PhNH₂, Me₂CO-HCO₂H, CCl₄(N₂), EtOH, etc. In the systems AcOH-H₂O, MeOH-H₂O, Me₂CO-AcOH, PhOH-Me₂CO, the max. corresponds to no stoichiometric ratio of the components and to no definite compd. An S-shaped ΔA curve, resulting from the predominance of the dissociation of an assoc. component along one part of the curve, and of compd. formation along another part, is exemplified by the systems SbCl₃-C₆H₅, SbCl₃-CHPh₃, and SbCl₃-C₆H₅, where, again, the max. corresponds to no stoichiometric ratio of the components.

N. Thom

CA

2

Classification of complex-forming elements and addends on the basis of energy characteristics. K. H. Vatsilyshskii (Ivanov Chem.-Technol. Inst.). Zhuravskii A.M. (J. Gen. Chem.) 20, 1401 7(1950). In the general case, the energy of formation ΔH of a complex ion from the gaseous central ion and the gaseous addends ("energy of addn.") is composed of electrostatic and covalent terms; specifically, if n is the no. of donor-acceptor covalent bonds in the complex ion, $\Delta H = I - nE - nD + U$, where I = total ionization potential, E = electron affinity of the addend, D = energy of the covalent bond between the central ion and the addend, and U = resonance energy of the given structure. On that basis, both complex-forming central elements and addends can be classified, roughly, in 4 groups: (1) "electrostatic," characterized by a high elec. charge, small radius r , high dipole moment, relatively low I , and high E ; examples of central atoms are Al^{3+} , Fe^{3+} , Zr^{4+} , Hf^{4+} , and of addends, F^- , H_2O , ROH , CO_3^{--} , SO_4^{--} ; (2) "covalent," characterized by high I , low E , low electrostatic characteristics; examples of central atoms are Au^+ , Hg^{2+} , Pb^{2+} , Bi^{3+} , Tl^+ , addends $S_2O_8^{--}$, I^- , CNS^- , Br^- , CSN, H_2 ; (3) "universal," characterized by high I , low E , high elec. charge and small r ; examples are Co^{3+} , Fe^{3+} , Rh^{3+} , Ir^{3+} , Cu^{2+} , and the addends CrO_4^{--} , Fe^{3+} , Rh^{3+} , CN^- ; (4) "intermediate," characterized by medium values of all energy characteristics; examples are Ni^{2+} , Zn^{2+} , Co^{2+} , Fe^{2+} , Ag^+ , Cu^+ , Cd^{2+} , and the addends NH_3 , $CaH_2(NH_2)_2$, NO_2^- , HCO_3^- . Phenomena of group selectivity in complex formation and differences of stability of complex ions in soln. can be interpreted from this point of view.

N. Thon

YATSIMIRSKIY, K. B.

CA

Formalopentammine salts of cobalt(III). K. B. Yatimirskii. Zhur. Obshchei Khim. (J. Gen. Chem.) 20, 1408-11 (1950). Two new complex salts of Co(III) were synthesized. $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]\text{I}$ (I), red crystals, was obtained with a 95% yield by 40-min. heating 5 g. of Co purpleochloride, $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}$, with 100 ml. of a concd. soln. of HCO_3K contg. approx. an 8-fold excess of HCO_3K , subsequent mixing of the cooled red soln. with an equal vol. of satd. KI, and washing the ppt. with ice water, aq. alc., and finally 90% alc. With a satd. soln. of NH_4NO_3 instead of KI, a red ppt. of $[\text{Co}(\text{NH}_3)_5\text{HCO}_3](\text{NO}_3)$ (II) was obtained in a 90% yield. The heats of reaction with a 0.26 M soln. of Na_2S at 25° were detd., for I, to be -3110 cal., and for II, to be -4560 cal./mole. The heats of soln. in H_2O were detd. to be 14780 and 16381 cal./mole, resp. Hence, and with the use of the thermochem. data of Bichowsky and Rossini, the standard heats of formation ΔH_{298}° of the solid salts were calcd. to be I -261.2, II -334.3 kcal./mole, and for the ion $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$ in aq. soln., -219.7 kcal./mole. For the gaseous ion $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$, the heat of formation was calcd. to be 194 kcal./mole with the aid of the Kapustinskii equation for the lattice energy, with the thermochem. radius of the ion assumed = 2.30 Å. Hence, the heat of the reaction $\text{Co}^{+++}(\text{gas}) + 5\text{NH}_3(\text{gas}) + \text{HCO}_2^-(\text{gas}) = [\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}(\text{gas}) + \text{IV}$ is $x - 357$ kcal., where x = heat of formation of the gaseous Co^{+++} . Consequently, the thermal stability of the gaseous $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$ is greater than the stability of all other acidopentammine Co(III) ions, with the exception of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$. The stability of these complex ions decreases in the order $\text{NO}_2^- > \text{HCO}_2^- > \text{CNS}^- > \text{I}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^-$. N. Thon

1ST AND 2ND ORDER		PROCESSES AND PROPERTIES INDEX	
1786		2	
<p>THE PROBLEM OF SOLUBILITY OF COMPLEX SALTS. K. B. Yatsimirskii. <i>Zhur. Obshch. Khim.</i> 20, 2133-8 (1950) Dec. (in Russian)</p>			
<p>Using a theoretical approach that has led to the discovery of certain regularities in the solubility of simple ionic compounds (Kapustinskii and Yatsimirskii, <i>Zhur. Fiz. Khim.</i> 22, 1271 (1948)), an analysis is made of fundamental factors that determine the solubility of complex salts, viz., dimensions of ions, their charges, and the presence of polar or hydrophilous groups in their compositions. Regularities are de-</p>			
<p>scribed permitting an explanation of differences in the solubility of certain groups of complex salts, and conditions are set forth under which difficultly soluble complexes can be obtained. It can be stated that in order to obtain a difficultly soluble compound of a given complex ion, or, more generally, of a given large ion ($r > 2 \text{ \AA}$), another sufficiently large ion of opposite sign, and with a maximal possible charge, must be selected, the sizes of both standing in a certain optimal relation to each other; the given ion must not contain hydrophilous groups, while a well-expressed polarity within that ion is desirable.</p>			
<p>ASH-SLA METALLURGICAL LITERATURE CLASSIFICATION</p>			
<p>GROUPS</p>		<p>REMARKS</p>	
<p>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100</p>		<p>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100</p>	

YATSIMIRSKIY, K. B.

Chem

Thermochemistry of complex compounds with ethylenediamine. K. B. Yatsimirskii and A. A. Astasheva. Chem. Tech. Inst., Lvov. Zhur. Obshchei Khim. (J. Gen. Chem.) 20, 2139-43 (1950).—Calorimetric measurements at 25° gave for the heats of the reaction of the complex salts with 1 N HCl the following values ($\text{en} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$): $[\text{Cd en}] \text{Cl}$ 46.43; $[\text{Cd en}] \text{Br}$ 39.2; $[\text{Ni en}] \text{Cl} \cdot 2\text{H}_2\text{O}$ 39.00; $[\text{Ni en}] \text{Br}$ 37.04; $[\text{Ni en}] \text{I}$ 35.41 kcal./mole. From $[\text{M en}] \text{X}_2 (\text{cryst.}) + 6\text{HCl aq.} \rightarrow \text{M}^{++} \text{aq.} + 3\text{en H}_2^{++} \text{aq.} + 6\text{Cl}^- \text{aq.} + 2\text{X}^- \text{aq.} + \text{Q}$, and detns. of the heats of soln., the heats of formation of the complex salts in the standard state were calcd. to: $[\text{Cd en}] \text{Cl}$ 168.8, $[\text{Cd en}] \text{Br}$ 149.0, $[\text{Ni en}] \text{Cl}$ 163.1, $[\text{Ni en}] \text{Br}$ 148.0, $[\text{Ni en}] \text{I}$ 119.6, $[\text{Ni en}] \text{Cl} \cdot 2\text{H}_2\text{O}$ 309.7, $[\text{Ni en}] \text{Br} \cdot 2\text{H}_2\text{O}$ 290.4, $[\text{Ni en}] \text{I} \cdot 2\text{H}_2\text{O}$ 259.9, $[\text{Cd en}]^{++} \text{aq.}$ 78.3, $[\text{Ni en}]^{++} \text{aq.}$ 81.6 kcal./mole. The energy, W , of binding of gaseous en by the gaseous metal ion M^{++} , to form the gaseous complex ion $[\text{M en}]^{++}$, is estd. from the lattice energy U of the cryst. complex salts, $[\text{M en}] \text{X}_2 (\text{cryst.}) = [\text{M en}]^{++} (\text{gaseous}) + 2\text{X}^- (\text{gaseous}) - U$, where U is calcd. by Kapustinskii's equation (C.A. 38, 5705'), with the thermochem. radii of all complex ions $[\text{M en}]^{++} = 2.7 \text{ \AA}$. This gives for W , Ni^{++} 283, Zn^{++} 372, Co^{++} 372, Fe^{++} 342, Cd^{++} 323 kcal./mole. The order of the heats of binding of 3 en by these ions is the same as that of the heats of binding of 6 NH_3 ; the latter are lower by 5-13 kcal. From the difference of the heats of formation of the anhyd. and the hydrated salts, the heats of hydration are calcd. to $[\text{Ni en}] \text{Cl} \cdot 2\text{H}_2\text{O}$ 10.3, $[\text{Ni en}] \text{Br} \cdot 2\text{H}_2\text{O}$ 5.9, $[\text{Ni en}] \text{I} \cdot 2\text{H}_2\text{O}$ 3.6. The abnormal increase of the heats of hydration from the iodide to the chloride can be explained by assuming hydration of the anion rather than the cation. N. T.

CA

The solubility of complex salts. K. B. Vatsimirskii
(Chem. Technol. Inst., Ivanovo). *J. Gen. Chem. U.S.S.R.*
20: 2213-17 (1950) (Engl. translation). See *C.I.* 43,
B. I. M.

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CM

Energetics of complex compounds. K. N. Yatsulyanskiy
(Chem. Technol. Inst., Ivanovo). Izv. Vses. Khim.
(Drugikh Mater., Inst. Obshch. i Neorg. Khim.,
Akad. Nauk S.S.R. No. 25, 6-28 (1971)).—An extensive
discussion of previous work (C.A. 42, 4944c, 1954).
M. Hosh

1951

Thermochemistry of the trans influence. K. H. Yee, *Smithsonian Chem. Technol. Inst.*, *Doklady Akad. Nauk S.S.S.R.* 74, 307-10 (1980). With the heat of formation of the hydrated Co^{++} ion assumed to be $\Delta H_{f, aq}^{\circ} = 22$ kcal. (from the free energy, with the entropy of the ion in soln. taken equal to that of Fe^{++}), the following heats of formation of the complex ion in soln. (from the hydrated central ion and addends) are calculated: $[\text{Co}(\text{NH}_3)_6]^{++}$ (I) 41.7; $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$ (II) 53.1; $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{++}$ (III) 53.1; $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]^{++}$ (IV) 45.0; $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^{++}$ (V) 53.1; $[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^{++}$ (VI) 53.0; $[\text{Co}(\text{NO}_2)_6]^{++}$ (VII) 53.0; $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$ (VIII) 50.2; $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)(\text{Cl})]^{++}$ (IX) 49.3; $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_2(\text{Cl})]^{++}$ (X) 45.0; $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_3(\text{Cl})]^{++}$ (XI) 47.0; $[\text{Co}(\text{NO}_2)_5(\text{Cl})]^{++}$ (XII) 47.0; $[\text{Co}(\text{NO}_2)_6]^{++}$ (XIII) 28.1 kcal. From these data, the heats of displacement of NO_2 by NH_3 are: V \rightarrow II, 0.0; VI \rightarrow II, -0.8; II \rightarrow I, -1.2; X \rightarrow IV, -0.6; IX \rightarrow III, -7.6; XII \rightarrow VI, +18.9; XI \rightarrow VI, +6.9; VI \rightarrow I, -2.0 kcal. Heats of displacement of NO_2 by H_2O are, V \rightarrow X, -7.5; II \rightarrow IX, -3.8; II \rightarrow III, -11.4; IX \rightarrow VII, -17.3 kcal. Heats of displacement of NH_3 by Cl^- : II \rightarrow IX, -3.8; I \rightarrow III, -10.2; III \rightarrow VII, -0.7; III \rightarrow VIII, -11.5. Displacement of NH_3 by H_2O : II \rightarrow X, -7.6; I \rightarrow IV, -6.9; displacement of H_2O by Cl^- : X \rightarrow IX, +3.7; IV \rightarrow III, -3.3 kcal. These figures illustrate the possibility of thermochem. measurement of the trans influence. In the case of Co^{++} complexes, the series is $\text{NO}_2^- > \text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^-$. The susceptibility to trans influence decreases in that order, i.e. the heat effect accompanying the

displacement of NO_2^- is greatest when the trans position is occupied by NO_2^- , somewhat smaller if it is occupied by NH_3 or H_2O , and smallest with Cl^- in the trans position. In the displacement of 2 NO_2^- , the thermal effect is greatest with XII, smaller with XI, and neg. with VIII in trans position to NO_2^- . The same rules apply to displacement of NH_3 and H_2O by Cl^- ; the heat is greater with NO_2^- in trans position to NH_3 or H_2O than with NH_3 or Cl^- in that position. This order is reversed in the displacement of Cl^- by NH_3 or H_2O by NO_2^- , and in the displacement of Cl^- by NH_3 or H_2O by NO_2^- . These facts can be interpreted by assuming that, of the two d-, one s-, and three p-bonds of the octahedron, the d-bonds are the most stable and the p-bonds the least stable, and that the different addends have unequal tendency to occupy a d bond. This tendency appears to decrease in the order $\text{NO}_2^- > \text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^-$. For NO_2^- , the bond strength differs greatly, depending on whether the NO_2 group is bound by p- or d-bonds; this difference is less pronounced for NH_3 and H_2O , and seems to disappear completely for Cl^- . This conclusion is borne out by the heats of formation ΔH of geometric isomers. Croco-ions, with one NO_2 group bound by a p-bond, the other by a d-bond, have a lower ΔH than fluo-ions, with both NO_2 groups d-bonded. In the case of praseo- and violeo-salts, the trans isomer, with the Cl^- ions bound by d- and p-bonds, has the higher ΔH , probably as a result of the ionogenic nature of the bond.

YATSIMIRSKIY, K. B.

Thermochemistry of complex compounds Moskva, Izd-vo Akademii nauk
SSSR, 1951. (Mic 53-843 Collation of the original: 250 p.

Microfilm T-14

183T24

USSR/Chemistry - Analytical Reactions and Reagents Jul/Aug 51

"Classification of Analytical Reactions and Reagents on the Basis of the Energy Characteristics of Ions," K. B. Yatsimirskiy, Ivanovo Chem-Technol Inst

"Zhur Analit Khim" Vol VI, No 4, pp 211-217

"Covalent characteristic" of given ion, or tendency of ion to form covalent bond (calcd as difference between ion's ionization potential and its heat of hydration), electron charge, and ionic radius provide data for classification of ions for analyt

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USSR/Chemistry - Analytical Reactions and Reagents (Contd) Jul/Aug 51

purposes. Gives tables of above values for many anions and gen rules for prediction of soly when particular anion and cation are present in soln.

183T24

YATSIMIRSKIY, K. B.

LC

Complex compounds with anions of aromatic sulfonic acids in the outer sphere. K. B. Yatsimirski, K. E. Pils, I. A. Stevinskaya, and V. V. Starostin (Chem.-Technol. Inst., Ivanovsk). Zhur. Obshchei Khim. (J. Gen. Chem.) 21, 480-90 (1951). Mixing 1% solns. of aromatic sulfonates (Na salts) with aq. solns. of $[Cr(NH_3)_6]Cl_3$ (I), $[Cr(NH_3)_4(NO_2)_2]$ (II), or $[Cr(CON_2H_2)_6]Cl_3$ (III) usually gave ppt. of the corresponding complex salts. *p*-Me₃C₆H₄SO₃Na gave with I and III ppt. having compns. of the type $[Cr(NH_3)_4(C_6H_4SO_3)_2]$. The soly. of the Co salt is 0.0037 mole/l. at 20°. Na sulfonate does not give ppt. 2,4-CIMeC₆H₃SO₃Na gives ppt. with I, II, and III; $[Cr(NH_3)_4(C_6H_3ClSO_3)_2]$, green; $[Cr(NH_3)_4(C_6H_3ClSO_3)_2]$, yellow; $[Cr(CON_2H_2)_4(C_6H_3ClSO_3)_2]$, yellow, soly. The 2-nitro analog gives ppt. with I, II, and III; $[Cr(NH_3)_4(C_6H_3NSO_3)_2]$, yellow, soly. 0.0087 mole/l. at 40°; $[Cr(CON_2H_2)_4(C_6H_3NSO_3)_2]$, green, soly. 0.0033 mole/l. at 20°. The 2-chloro-5-nitro analog also gives ppt. with I, II, and III; $[Cr(NH_3)_4(C_6H_3ClNSO_3)_2]$, yellow; $[Cr(CON_2H_2)_4(C_6H_3ClNSO_3)_2]$, green. Na 3-carbazolesulfonate gives ppt. even in rather dil. solns. with I, II, and III. Even less sol. are the salts of 6-nitro-3-carbazolesulfonic acid; $[Co(NH_3)_4(C_6H_3N_2SO_3)_2]$, yellow; $[Cr(CON_2H_2)_4(C_6H_3N_2SO_3)_2]$, yellow; poorly sol. salts also form with derivs. of Cu, Zn, Ni, and Cd. Especially poorly sol. are salts of alizarinsulfonates; salts with I and II are especially mentioned but are not further characterized.

Generally, the soly. declines with increased size of the anion and with introduction of polar groups into it. Introduction of OH, NH₂, or CO₂H groups into the sulfonate radical sharply raises the soly. of the complex salts. Sepn. of some sulfonic acids by such means may be feasible. G. M. K.

Unsaturated cyclic hydrocarbons and their halogen derivatives. X. Transformation of unsaturated cyclic hydrocarbons.

184T33

YATSIMIRSKIY, K. B.

USSR/Chemistry - Analytical

Feb 51

"Problem of the Variation of Free Energy and Entropy in Reactions of Formation of Complexes," K. B. Yatsimirskiy, Chair of Analyt Chem, Chemicotech Inst, Ivanovo

"Zhur Fiz Khim" Vol XXV, No 2, pp 221-223

Advances hypothesis, based on entropy data for RO_2^- ions (i.e., CO_3^{2-} , MO_4^{2-}), that only thermochem ratios determine entropy of single-type complex ions (i.e., those having equal number of same groups combined to cen ion). Shows difference between heat effect and free energy to be const in single-type

184T33

USSR/Chemistry - Analytical (Contd)

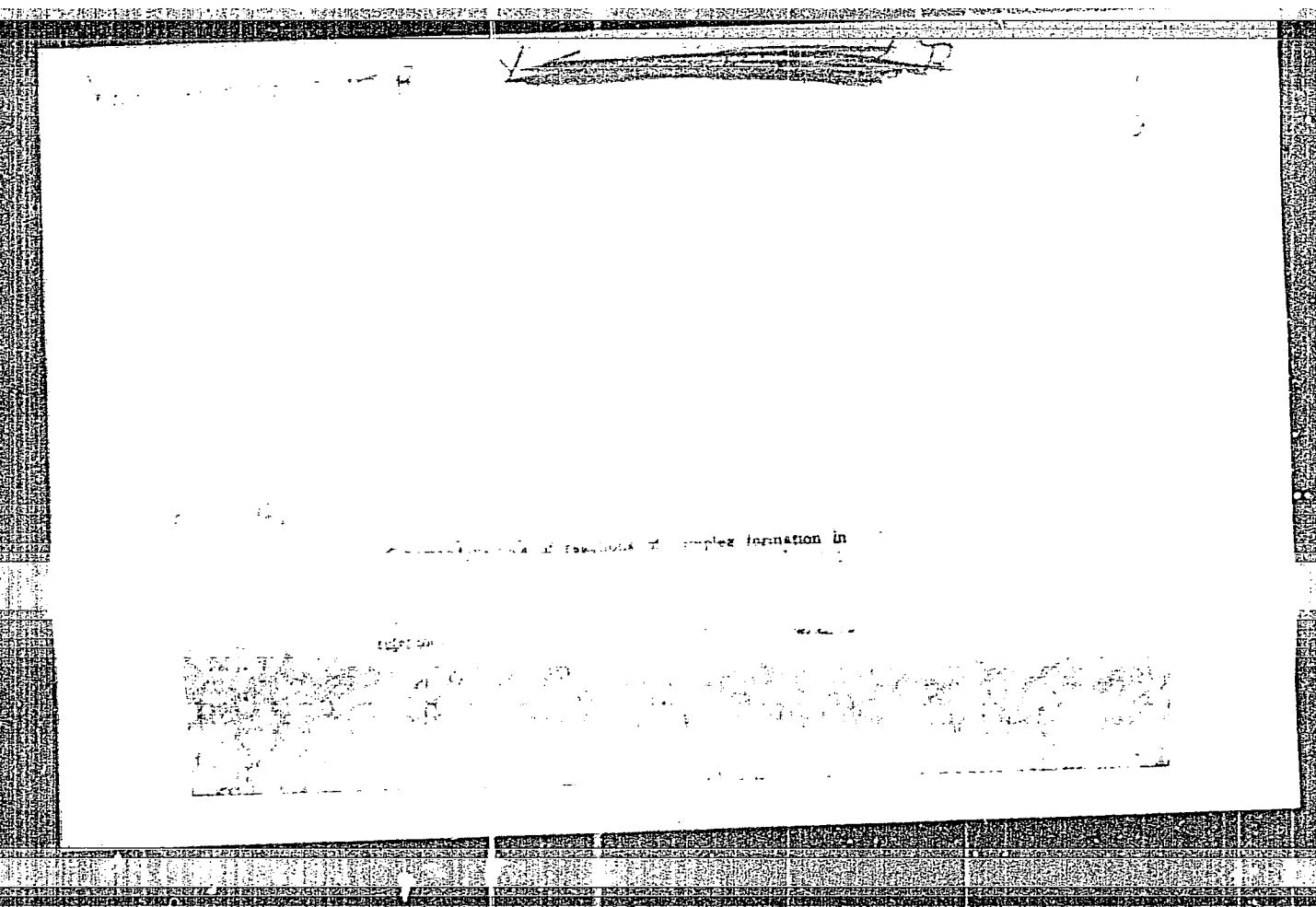
Feb 51

complex formation. Arranges anions and cations by decreasing stability, latter assumed to be detd by difference between ionization potential of cen atom and heat of hydration of ion formed.

184T33

CA

Stability constants of some complex compounds of lead.
N. B. Yatsimirskii (Chem.-Tech. Inst., Ivanovo). *Zhur.*
Pril. Khim. 25, 475-9 (1951).—Earlier theoretical predictions
(C.A. 43, 6110f) concerning the relative stability of com-
plexes in soln. are verified by expts. leading to the detn. at
25° of the stability const. $K_1 = \frac{[Pb(S_2O_3)_2^{2-}]}{[Pb^{2+}][S_2O_3^{2-}]^2}$ and $K' = \frac{[Pb(CNS)_2]}{[Pb^{2+}][CNS^-]^2}$. The values $K_1 = 1.35 \times 10^8$
and $K_2 = 2.23 \times 10^8$ are obtained by measuring the soly. of
 PbS_2O_3 in aq. solns. of $Na_2S_2O_3$. The soly. product of PbS_2O_3
is also calcd.: 3.90×10^{-1} . The value $K' = 0.8$ is found
by measuring the soly. of $Pb(CNS)_2$ in aq. solns. of $KCNS$.
The soly. product of $Pb(CNS)_2$ is 2.00×10^{-1} . Finally, the
stability const. $K'' PbBr_2$ is estd. from the data of Burrage
(C.I. 20, 3422); it is approx. 2×10^3 . These values of K_1 ,
 K_2 , K' and K'' confirm the theory. Michel Boudart



CP

The periodic law of D. I. Mendeleev and the stability of complex compounds. A. A. Grinberg and K. B. Yatsimskii. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1952, 211-17. —The tendency to complex formation is characterized quantitatively by the energies of formation of the gaseous complex ions, and by the instability const. K of the complex; the latter magnitude actually expresses the difference of the stability of the complex ion and of the corresponding aquo ion. From a thermodynam. cycle involving the formation of a complex ion $[MA_n]^{+n}$ from $M^{+n} + nA$, the heat is $\Delta H = (W_1 - W_2) + (L_1 - L_2) + n(\lambda_1 - \lambda_2)$, where W_1 and W_2 are the energies of addn. of H_2O and of A , resp., to the gaseous M^{+n} , L_1 and L_2 are the heats of hydration of $[MA_n]^{+n}$ and $[M(H_2O)_n]^{+n}$, resp., and λ_1 and λ_2 the heat of evapn. of H_2O and of hydration of A , resp. The latter term being const., $\Delta H \approx (W_1 - W_2) + C$ the middle term approx. const., $\Delta H \approx (W_1 - W_2) + C$ (const.), and $RT \ln K \approx (W_1 - W_2) + C$ (const.). This gives the relation between the 2 characteristics of the tendency to complex formation. This relation is verified by data for $[Mg(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Ni(NH_3)_6]^{2+}$, $[Co(en)_3]^{3+}$, $[Ni(en)_3]^{2+}$, and $[Zn(en)_3]^{2+}$. In application to ions with an inert-gas structure of the outer electron shell, but different charge and radius, this leads to the conclusion

that the stability of complexes increases from left to right in the period and decreases from top to bottom in the groups of the periodic system. For ions with 18-electron shells, the complex stability ought to decrease with increasing at. no. in the groups if the bond is predominantly ionic; with predominantly covalent bonding, elements of the 6th period should form particularly stable complexes. As a result of the 2 antagonistic factors, the heat of formation of gaseous complex ions within a subgroup may pass through a min.; examples are, for complex ions $[M(NH_3)_6]^{+n}$, $M = Cu$ 131, Ag 104, Au 140 kcal./mole, and for ions $[M(NH_3)_6]^{+n}$, $M = Zn$ 301, Cd 311, Hg 378 kcal./mole. The same is found for the free-energy change $\Delta F = RT \ln K$ of formation of complex ions in aq. soln. The more pronounced is the covalent character of the bond, the more marked is the increase of the stability (ΔF) of the complex ions from top to bottom; this is illustrated by comparison of ΔF for complex chlorides, bromides, and iodides, the latter showing the most marked change of ΔF from Cu to Au or from Zn to Hg , and the chlorides the least marked. In series of complex ions formed by central ions with the same charge, but with different outer-electron shell structures, the complex sta-

pull

YATSIMIRSKIY, K.B.; ASTASHEVA, A.A.

Slightly soluble complex compounds of thiourea and their use in analysis.
J. Anal. Chem. U.S.S.R. 7, 45-9 '52 [Engl. translation].
(CA 47 no.19:9849 '53)

YATSIMIRSKIY, K.B.

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Analytical Chemistry

Thermodynamic criteria for the applicability of chemical
reactions to volumetric analysis. K. B. Yatsimirskii
(Ivanovo Chem. Tech. Inst.). *J. Appl. Chem.* 1952, 5, 23-24 (Engl. translation).—*See C.A.* 47, 1529b.
H. L. H.

YATSIMIRSKIY, K. B., SHUTOV, A. A.

Mercury Compounds

Instability constants of complex mercury-iodide compounds. Zhur. fiz. khim. 16 no. 6, 1952

Monthly List of Russian Accessions. Library of Congress. November, 1952, Unclassified.

YATSIMIRSKIY, K.B.

③

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
Inorganic Chemistry

Some ternary complexes of copper and silver. K. B. Yatsimirskii and V. E. Panova (Vologda Inst. Chem. Technol.). *J. Gen. Chem. U.S.S.R.* 22, 1325-33 (1952) (Engl. translation); *Zhur. Otskhet Khim.* 22, 1284-9 (1952).—When halides of Cu (I) and Ag dissolve in solns. of $S_2O_3^{2-}$, mixed complexes of the type $[MeXS_2O_3]^{--}$ are formed. The solubilities of CuI and CuCNS in thio-sulfate solns. were measured at various temps., and the stability consts. were calcd. for the resultant $[CuS_2O_3]^{--}$ and $[Cu(CNS)S_2O_3]^{--}$ as 3.1×10^{-11} and 1.3×10^{-11} , resp. On the basis of literature data for the solubilities of Ag halides in thiocyanate and thiosulfate solns., the following stability consts. were calcd.: $[Ag(CNS)_3]^{--}$, $1.0 \pm 0.5 \times 10^{-11}$; $[Ag(CNS)_2]^-$, 7.1×10^{-11} ; $[AgClS_2O_3]^{--}$, 0.7×10^{-11} ; $[AgBrS_2O_3]^{--}$, 4.1×10^{-11} ; $[AgIS_2O_3]^{--}$, 2.7×10^{-11} .

Bernard Rubin

9-2-54
JRP

YATSMIRSKIY, K.B.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
General and Physical Chemistry

The absolute contraction constant and the periodic law
I. I. Zaslavskii and K. B. Yatsmirskii. *J. Gen. Chem.*
(U.S.S.R.) 22, 1753-C (1952) (Engl. translation).—See C.A.
47, 1098d. H. L. H.

(2) Chem

9-2-54
JYP

YATSIMIRSKIY, K. B.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
General and Physical Chemistry

②
Thermochemistry of nickel-ammonia complexes in
aqueous solution. V. K. B. Yatsimirskii and L. M. Grafova.
J. Gen. Chem. (U.S.S.R.) 22, 1705-9(1952)(Engl. transla-
tion).—See C.A. 47, 2030c. H. L. H.

YATSIMIRSKIY, K. B.

Compounds, Complex

"Thermochemistry of complex compounds."
Reviewed by O. Ye. Zvyagintsev. Zhur. prikl.
khim, 25, No. 7, 1952.

Monthly List of Russian Accessions, Library of Congress, November 1952, UNCLASSIFIED.

YATSIMIRSKIY, K. B.

USSR/Chemistry - Cadmium and Lead
Compounds

Feb 52

"Entropy Changes During Formation of Complex Halides
in Aqueous Solutions," K. B. Yatsimirskiy, A. A.
Astasheva, Ivanovo Chem-Technol Inst

"Zhur Fiz Khim" Vol XXVI, No 2, pp 239-243

Calcd entropy changes occurring during formation of
some halide and cyanide complexes as well as std
entropies for 11 complex ions and mols in aq soln
(2 tables). Detd heats of mixing of $Cd(NO_3)_2$ and
 $Pb(NO_3)_2$ solns with KI solns. On the basis of exptl
data, calcd heat effects of formation of ions

211749

CdI_4^- , PbI_4^- , CdI_3^- in aq soln as well as contin-
gent entropy changes. Shwed that published re-
sults on heats of formation of $CdCl_2$ and PbI_4^- are
in need of correction.

211749

Inorganic Chemistry

CA

Constants of instability of mercury-iodine complex compounds. (C. B. Yatsimirskii and A. A. Shutov (Chem. Technol. Inst., Ivanovo). *Zhur. Fiz. Khim.* 26, 842-7 (1952).) The soly. S of HgI_2 in 0.026 M , 0.090 M , 0.268 M , 0.503 M , 0.844 M , 1.058 M , 1.345 M , and 1.551 M $Hg(NO_3)_2$ at 25° is 49, 85, 276, 443, 684, 928, 1290, and 1538×10^{-4} mole/l. Except the last two, these values can be represented by $S = 0.0224 c^{1/2} + 0.0895 c^{1/4}$, in which c is the concn. of Hg^{2+} , complete dissociation being assumed. The increase of S with c cannot be explained by the ionic strength I of the soln., as S increases with c also when I remains constant (in solns. of $Mg(NO_3)_2$ and $Hg(NO_3)_2$ at $I = 6$). As S contains terms in $c^{1/2}$ and $c^{1/4}$, the increase of S is due to formation of $[HgI]^+$ and $[HgI_2]^0$ ions. From the above equation $A_1K_1 = 0.0224$ and $A_2K_2 = 0.0895$; A_1 is the soly. product of HgI_2 ($\approx 10^{-18}$), $K_1 = 7.06 \times 10^{-10}$ is the instability constant of $[HgI]^+$, and $K_2 = 1.77 \times 10^{-11}$ is the instability constant of $[HgI_2]^0$. The soly. was determined in the usual manner and also by titrating $Hg(NO_3)_2$ solns. with KI to opalescence. J. J. Bikerman

YATSIMIRSKIY, K. P.

Investigation of bismuth halide complexes by the solubility method. $K \cdot 10^{-4}$ for $(\text{BiCl}_4^-)/(\text{H}^+)$ and for the corresponding bromide method. $K \cdot 10^{-4}$ for $(\text{BiBr}_4^-)/(\text{H}^+)$. The curve $\log S$ vs. $\log [\text{HNO}_3]$ for BiONO_2 is a straight line at low HNO_3 concn., and in this range the

the reaction for all concns. proceeds by 1. The curves for variable KX concns. are curved lines. A series of assumptions and limitations leads to different values of K (4.5, 4.5, 4.5) and those of Smith provide a graphic method for the calculation of K . The curves for variable KX concns. are curved lines. A series of assumptions and limitations leads to different values of K (4.5, 4.5, 4.5) and those of Smith provide a graphic method for the calculation of K . The curves for variable KX concns. are curved lines. A series of assumptions and limitations leads to different values of K (4.5, 4.5, 4.5) and those of Smith provide a graphic method for the calculation of K .

YATSIMIRSKIY, K. B.

4

The calculation of the dissociation constants of stepwise complex formation from polarographic data. K. B. Yatsimirskiy (Chem. Technol. Inst., Ivanovo). *Sbornik State Obshchest. Nauch. Akad. Nauk S.S.S.R.* 1, 193-9 (1963).—The standard equations used for the calcul. of equil. consts. from polarographic data are derived on the assumption of a single equil. reaction, $MX_{p-1}^{n-p+1} \rightleftharpoons M^{n+} + pX^{q-}$. When stepwise complex formation occurs, it is necessary to add another equil.: $MX_{p+1}^{n-p-1} \rightleftharpoons MX_{p-1}^{n-p+1} + X^{q-}$ (for notations cf. Stromberg, et al., *C.A.* 43, 5691e). This leads to relations that, upon differentiation and limitation to the case where the concn. of both complex ions is the same, become $\partial \Delta E / \partial \log C_0 = A(p + 0.5)$ and $\Delta E = A(\log C_0^{p+1} - \log K_{p+1} + \log 2)$, where $A = 0.059/n$. The tangent for $p = 1, 2$, etc., is drawn to the ΔE vs. $\log c$ curve, and thus p , ΔE , and $\log C_0$ are obtained. Dissocn. consts. of known complexes calcd. by this method agree with, or are of the same order of magnitude as, those calcd. by the older, simplified method. I. Benacowitz

Sm
L

YATSIMIRSKIY, K.B.

Stability of different degrees of oxidation of the elements.

K. B. Yatsimirskiy (Chem. Technol. Inst., Leningrad)
USSR State Technical Film Acad. News of USSR, 1963, No. 1953. The question of the stability of the oxidation state of an element in the presence of a reducing agent is discussed. It is shown that the stability of the oxidation state of an element in the presence of a reducing agent is determined by the rate of the reaction of the element with the reducing agent. The rate of the reaction of the element with the reducing agent is determined by the rate of the reaction of the element with the reducing agent.

On the stability of the oxidation state of an element in the presence of a reducing agent. The question of the stability of the oxidation state of an element in the presence of a reducing agent is discussed. It is shown that the stability of the oxidation state of an element in the presence of a reducing agent is determined by the rate of the reaction of the element with the reducing agent. The rate of the reaction of the element with the reducing agent is determined by the rate of the reaction of the element with the reducing agent.

YATSIMIRSKII, K. B.

Chemical Abst.
Vol. 48, No. 4
Feb. 25, 1954
Analytical Chemistry

Chem 4
(2)

The nature of the so-called "weighting effect." K. B. Yatsimirskii (Ivanov Chem. Technol. Inst.), *Zhur. Anal. Khim.* 8, 314-20 (1953).—The "weighting effect" first proposed by Feigl (*C.A.* 19, 1108) according to which an increase in the mol. wt. of a reagent increases the sensitivity of the latter toward a given reaction is not strictly true. The analysis outlined in *C.A.* 43, 1241i and 45, 3089e is applied here to org. reagents. It is shown that addn. of various groups into an analytical reagent causes a change in the free energy of its lattice. Replacement of H in a C—H group by some other group causes a change in the log of soly. ($\Delta \log S$) by approx. the same value. For OH, $\Delta \log S \sim 1.5$, i.e. the soly. increases approx. 30 times. For other groups $\Delta \log S$ is for CH_3 , -0.60 , C_2H_5 , -2.1 , Cl -0.4 , Br -0.5 , and I -1.0 . The effect of added CH_3 groups was studied on Li, Ca, and Ba fatty acid salts. For these salts $-\Delta \log S/n$ was calcd. where n is the no. of CH_3 groups. Each addn. CH_3 caused the log S to decrease by an av. of 0.25. Addn. of aromatic rings caused a greater decrease in the soly. Addn. of hydrophobic groups causes a decrease in the soly. of the ppt. but at the same time reduces the soly. of the reagent which leads to a reduction of its sensitivity. M. Haseh

YATSIMIRSKIY, K.B.

Stability of complex compounds in aqueous solutions. Uspekhi Khim.22,
410-44 '53. (MLRA 6:4)
(CA 47 no.19:9841 '53)

YATSIMIRSKIY, K.B

U S S R

7. Cell and Ionization potentials K. A. Yasumura

[illegible]

L. F. Casey

YATSIMIRSKIY, K.B.; GRAMOVA, Z.M.

Thermochemistry of cuprammonium complexes in water solution. Zhur.ob.
khim. 23 no.5:717-720 My '53. (MLRA 6:5)

1. Ivanovskiy khimiko-tehnologicheskii institut.
(Thermochemistry) (Compounds, Complex)

YATSIMIRSKIY, K.B.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Inorganic Chemistry

3
②
Nickel-dimethylglyoxime complexes. K. B. Yatsimirskiy and Z. M. Gralova. *Zhur. Obshchei Khim.* 23, 835-41. (1953).—The reaction between NiSO_4 and dimethylglyoxime in ammoniacal soln. in the presence of atm. O_2 yielded a colored (I) and a colorless (II) complex compd. The ratio of Ni:dimethylglyoxime in I was 1:3; in II, 1:1. The calcd. equil. const. checked well with the exptl. obtained by measuring the optical density of I at different concns. A. P. Kotloby

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11-5-54

YATSIMIRSKIY, K. B.

Instability constants of iodide-cadmium and iodide-lead complexes. K. B. Yatsimirskiy and A. A. Shutov (Chem. Technol. Inst. Ivanovo). *Zhur. Fiz. Khim.* 27, 782-9 (1953); cf. *C.A.* 46, 11602d. — The calcd. instability const. of the complex ions $(CdI)^{+++}$, $(CdI)^{++}$, $(PbI)^{+++}$, and $(PbI)^{++}$ at 25° were 8.16×10^{-4} , 8.41×10^{-4} , 3.18×10^{-4} , and 5.05×10^{-4} , resp., by measurement of the soly. (S) of PbI_2 in aq. solns. of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ of various concns. S depended on the cation concns. according to the empirical equations $S_1 = 0.037[Cd]^{1/2} + 0.0236[Cd]^{1/2}$ and $S_2 = 0.0032[Pb]^{1/2} + 0.00076[Pb]^{1/2}$. The calcd. relative activity coeffs. (γ) of PbI_2 in aq. solns. of Ca, Mg, and Zn nitrates are tabulated for concns. of the latter from 0.2 to 2.4M; values of γ for PbI_2 in satd. aq. soln. are 0.225, 0.309, and 0.319, resp., where γ for PbI_2 in satd. aq. soln. is arbitrarily equal to unity. The soly. product of PbI_2 , calcd. from exptl. data by the method of Kapustin (C.A. 38, 2870¹), is 1.05×10^{-4} .
I. W. Inweherv. Jr.

YATSIMIRSKIY, K.B.

Thermochemistry of anthracenes. K. B. Yatsimirskii
 and V. V. Khramov (Chem. Technol. Inst. Ivanovo).
 Dokl. Akad. Nauk SSSR 27: 100 (1971) (Engl. transl. in J. Chem. Phys. 45: 6354, 1966).
 The heat of reaction (H) of a 24M HCl soln. (I) with cryst.
 anthracene (II) to form (III) is -16.00 kcal./mole. The heats of
 formation (H_f) of (III) and (IV) are -16.00 and -13.42 kcal./mole, resp.
 The heat of formation (H_f) of anthracene (II) was measured in an illustrated microcalorimeter
 at 25° . Values of H_f for II to VIII are -16.00 , -11.11 ,
 -14.89 , -11.58 , -8.60 , -8.46 , and -13.42 kcal./mole,
 resp. Measured values of the heat of soln. at 25° in 1 of
 cryst. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, FeCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$,
 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ are 5.25 , 11.0 ,
 13.50 , 8.4 , and 1.7 kcal./mole, resp. The
 heat of formation (H_f) of anthracene (II) is -16.00 kcal./mole.
 where $A_d = 20.0$ kcal./mole, $A_1 = 1.0$ kcal./mole, and $A_2 = 1.0$ kcal./mole.
 The calculated lattice energies of II to VIII have the
 value $A + A_1$, where $A = 62.0$, 64.0 , 67.0 , 68.4 , 69.4 ,
 682.3 , and 627.1 kcal./mole, resp., and A_1 is the heat of
 formation of the An anion. J. W. Loweberg, Jr.

YATSIMIRSKIY, K. B.

USSR/Chemistry - Cadmium, Palladium, Oct 53
and Bismuth Compounds

"Thermochemistry of Complex Thiourea Compounds
in Aqueous Solutions," K. B. Yatsimirskiy, A. A.
Astasheva, Ivanovo Chem-Technol Inst

Zhur Fiz Khim, Vol 27, No 10, pp 1539-44.

Detd the heat of mixing of solns of the salts
 AgNO_3 , $\text{Hg}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, CdBr_2 , CdI_2 , $\text{Pd}(\text{NO}_3)_2$,
 $\text{Bi}(\text{NO}_3)_3$, and CuCl_2 with thiourea solns of dif-
ferent concns. Detd the changes of enthalpy

272T12

and entropy in connection with the formation of
complex ions from Ag^+ , Cu^+ , Cd^{2+} , and Pb^{2+} with
thiourea. Estimated the constant of instability K of
 $[\text{Hg}(\text{thiourea})_4]^{2+}$ to be 1.1×10^{-33} on the basis
of thermochemical data.

272T12

YATSIMIRSKIY, K.B.

USSR.

Use of dimethylphenylbenzylammonium as reagent for large anions. K. B. Yatsimirskiy and Z. I. Bergovoyshchen-skaya. *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 5(8) 90-3 (1954); cf. Emde, C.A. 3, 2470. The $\text{Me}_2(\text{Ph})(\text{PhCH}_2)_2\text{N}^+$ (I) ion was added to solns. of different anions. I pptd. CrO_4^{--} , $\text{S}_2\text{O}_8^{--}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, and iodide. Sensitivity of these reactions was detd. The crystals were photographed. A 1M soln. of ICl was mixed with 0.5M solns. of salts of the anions. With $\text{S}_2\text{O}_8^{--}$ white dendrites pptd. from concd. solns. (above 0.5%). Dil. solns. gave crystals. A 1M ICl soln. did not form a ppt. in solns. contg. <0.1% $\text{S}_2\text{O}_8^{--}$ but when a ICl crystal was added to 1 drop of such dil. $\text{S}_2\text{O}_8^{--}$ soln., crystals of $\text{I}_2\text{S}_2\text{O}_8$ formed rapidly. Min. concn. was 1:2000, detectable min. 0.5 γ (vol. of drop is 0.001 ml.). Soly. of $\text{I}_2\text{S}_2\text{O}_8$ increased greatly by heating. The salt was recrystd. from hot H_2O , dried over H_2SO_4 , and analyzed for S and N. With $[\text{Fe}(\text{CN})_6]^{4-}$ yellow crystals, $\text{I}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ formed. Min. concn. was 1:2000, detectable min. 0.5 γ . Compn. was confirmed by N and $[\text{Fe}(\text{CN})_6]^{4-}$ detns. With CrO_4^{--} yellow crystals with an unusual form pptd. from very dil. soln. Min. concn. was 1:2000, detectable min. 0.88 γ . Analysis for CrO_4^{--} confirmed the formula I_2CrO_4 . With $[\text{Fe}(\text{CN})_6]^{3-}$, ICl gave a ppt. only in the presence of acid. These fine greenish cubes are much less sol. in H_2O than the ferricyanide salt. Min. concn. was 1:17,000, detectable min. 0.058 γ . Detn. of N and $[\text{Fe}(\text{CN})_6]^{3-}$ confirmed the formula $\text{I}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. From iodide solns. a crystal of ICl pptd. I iodide as confirmed by analysis. Min. concn. was 1:400, detectable min. 2.5 γ . Eurlilla Mayerle

USSR/Chemistry

Card 1/1 : Pub. 145 - 5/10

Author: APPROVED FOR RELEASE: 09/19/2001 CIA-RDP86-00513R001962310007-2"

Title : Energy characteristics and analytical classification of ions

Periodical : Zhur. anal. khim. 9/5, 282-292, Sep-Oct 1954

Abstract : The basic energy characteristics of ions, which determine mainly their behavior in a solution and the electro-affinity of the ion in an aqueous solution, are explained. Judging by the magnitude of electro-affinity all cations can be divided into three groups; ions with low electro-affinity forming water-soluble sulfides; ions with mean electro-affinity values forming sulfides soluble in acids but not in water, and ions with high electro-affinity forming non-soluble sulfides. All three groups belong to mono-, di- and tri-charge ions with an electro-affinity of 30, 70 and 190 kcal. Five USSR references (1950-1952). Tables.

Institution :

Submitted : November 26, 1953

YATSIMIRSKIY, K. B.

USSR/Chemistry

Card 1/1 Pub. 151 - 10/36

Authors : Yatsimirskiy, K. B., and Yasinskene, E. I.

Title : The kinetics of aquation of Cr urea complexes

Periodical : Zhur. ob. khim. 24/1, 55-61, Jan 1954

Abstract : The constants of the rate of reaction leading to the aquation of hexaurea-chromion in an aqueous solution were measured at 30, 40, 50 and 60° temperatures. The activation energy was computed. The rate of reaction of hexaurea-chromion activation was also investigated by an optical method and the results are listed. Seven references: 4-USA; 2-USSR and 1-German (1903-1952). Tables; graphs.

Institution : The Chemical-Technological Institute, Ivanovo

Submitted : September 14, 1953

YATSIMIRSKIY, K. B.

USSR/Chemistry

Card 1/1 : Pub. 151 - 5/42

Authors : Yatsimirekiy, K. B.

Title : Factors determining the stability of certain complex compound groups in aqueous solutions

Periodical : Zhur. ob. khim. 24/9, 1498-1507, Sep 1954

Abstract : The effect of increased central ion charge on the stability of complexes in aqueous solutions, especially in the case of addenda-anions with small radii or high charges, is explained. The stability of complexes with large addenda increases with the increase in radius of the central ion; the stability of complexes with small addenda and amino-acids decreases with increase in radius of the complex forming cation. The polarizing effect of isochoric ions was characterized by means of instability constants. Fifteen references: 4-USSR; 11-USA (1948-1953). Tables; graphs.

Institution : Chemical Technological Institute, Ivanov

Submitted : March 25, 1954

YATSIMIRSKIY, K.B.

USSR/ Chemistry - Physical chemistry

Card 1/1 Pub. 147 - 6/26

Authors : Yatsimirskiy, K. B., and Shutov, A. A.

Title : On the thermochemistry of certain iodide complexes

Periodical : Zhur. fiz. khim. 28/1, 30-35, Jan 1954

Abstract : The change in the heat content and entropy which occurs during the formation of complex ions $[HgI]^+$, $[CdI]^+$ and $[PbI]^+$ was established from the experimental data regarding the heats of blending KI solutions with $Hg(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ solutions. The specific heats of these solutions were established. The heats of formation of the iodide complexes were estimated on the basis of the heats of decomposition of solid complex $[Ag_3I](NO_3)_2$ and $[HgI]NO_3$ salts with water and Na_2S solutions. Six references 5-USSR and 1-French (1876-1953). Tables.

Institution : The Chemical Technological Institute, Ivanovo

Submitted : February 16, 1953

YATSIMIRSKIY, K.B.

GRINBERG, A.A. (Leningrad); BABAYEVA, A.V. (Moscow); YATSIMIRSKIY, K.B. (Ivanovo); GOREMYKIN, V.I. (Moscow); BOLIY, G.B. (Moscow); FIAL-KOV, Ya.A. (Kiyev); YAKSHIN, M.M. (Moscow); KEDROV, B.M. (Moscow); GEL'MAN, A.D. (Moscow); FEDOROV, I.A. (Moscow); MAKSIMYUK, Ye.A. (Leningrad); VOL'EENSHTEYN, M.V. (Leningrad); ZHDANOV, G.S. (Moscow); PTITSYN, B.V. (Leningrad); ABLOV, A.V. (Kishinev); VOLSHTEYN, L.M. (Dnepropetrovsk); TROITSKAYA, A.D. (Kazan'); KLOCHKO, M.A. (Moscow); BABAYEVA, A.V.; TRONEV, V.G. (Moscow); RUBINSHTEYN, A.M. (Moscow); CHERNYAYEV, I.I.; GRINBERG, A.A.; TANANAYEV, I.V.

Explanation of the transeffect. Izv.Sekt.plat.i blag.met. no.28:
56-126 '54. (MLBA 7:9)

(Compounds, Complex) (Platinum)

YATSIMIRSKIY, K. B.

USSR/ Chemistry Physical chemistry

Card : 1/1 Pub. 11/7 - 17/25

Authors : Yatsimirskiy, K. B., and Zolotarev, E. K.

Title : On the thermodynamics of oxalate complexes

Periodical : Zhur. fiz. khim. 28/7, 1292 - 1298, July 1954

Abstract : Experimental data on the thermodynamics of oxalate complexes. The heat of blending solutions of homologous salts, with potassium and ammonium oxalate solutions, was determined for the purpose of estimating the enthalpy changes of such complexes. The instability constants of complex ions: $Mn, Co, Ni, Cu, Zn (C_2O_4)_2^{2-}$ and $Fe (C_2O_4)_3^{3-}$, were determined. Nineteen references: 8 USA; 7 USSR; 1 Italian and 3 German (1903 - 1952). Tables; graph.

Institution : Chemical-Technological Institute, Ivanov

Submitted : November 16, 1953

~~YATSKINER, K. B.~~

DATE: 10/10/80

1. 10. A new method for the estimation of

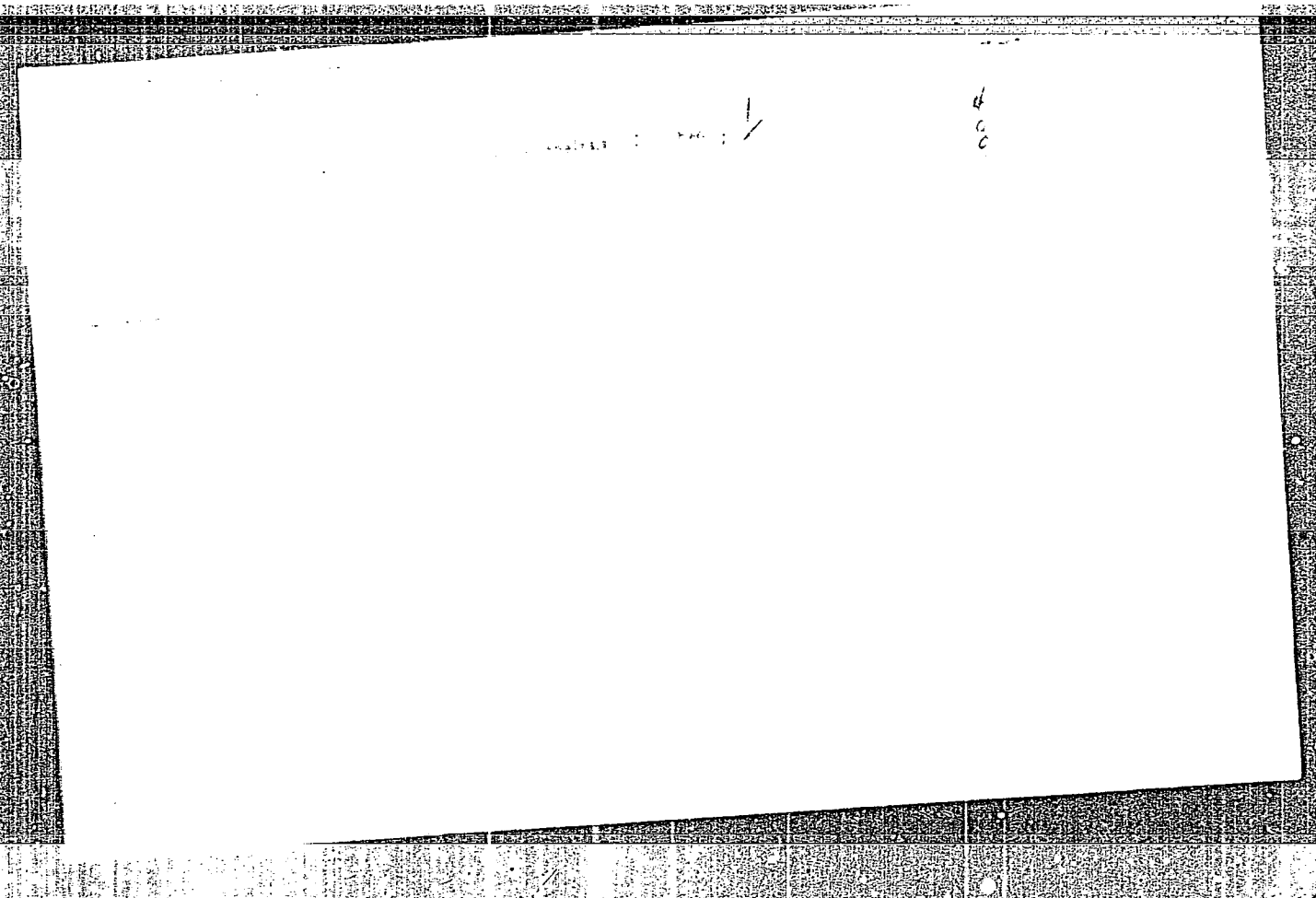
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YATSIMIRSKIY, K. B.

✓ Quantitative characteristics which determine the suitability of complex compounds for volumetric analysis. Chik. B. Yatsimirskiy (Int. Chem. Technol., Leningrad. Zhur. Anal. Khim. 10, 64-9(1955); J. Anal. Chem. U.S.S.R. 10, 85-9(1955)(Engl. translation).—In titration of complex-forming metals and in titration with such metals the max. degree of accuracy is detd. by the disocn. const. of the complex formed and by the initial concns. of the reactants. The accuracy of a titration is considered to be detd. by the ratio of the concn. of the given substance at the equivalence point to its initial concn. (cf. C.A. 47, 16295). The inverse logarithm of this ratio, designated by pT , is referred to as the index of titration accuracy. For a reaction of the type $M + A \rightleftharpoons MA$ a relation contg. pK (the inverse log of the disocn. const. of MA) is derived, under the assumptions that the initial concns. of M and A are equal and that the changes in vol. upon titration are negligible. Where disocn. occurs in more than 1 step, the equation is somewhat more complex. The min. pH at which a titration with a certain degree of required accuracy can be carried out can be calcd. Fixing or masking accompanying elements into complexes is essential in certain cases of titration. The completeness of masking is detd. by the ratio of the equil. consts. of the masked and masking reactions and by the concns. of the reactants. A set of equations is derived which express the completeness of masking. In certain procedures of volumetric analysis the sought ion is first converted into a complex ion and then pptd. The applicability of this method depends primarily on the sol. product of the complex salt formed. Conditions for suitability of colored end-point indicators are derived. M. Hoosh.

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2



APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

Use of complements in analytical chemistry

YATSIMIRSKIY, K.B.

Application of complexons in analytical chemistry. II.
Lab. 21. 1276-83(1966)

YATSIMIRSKIY, K.B.

VASIL'YEV, V.P.; YATSIMIRSKIY, K.B.

On E.A.Ukshe and A.I.Levin's article "Composition and properties of a complex electrolyte in a copper-pyrophosphate bath." Zhur. ob.khim.25 no.6:1233-1235 Je '55. (MIRA 8:12)

1. Ivanovskiy khimiko-tekhnologicheskii institut.
(Electrolytes) (Ukshe, E.A.) (Levin, A.I.)

YATSIMIRSKIY, K.V. (Ivanovo)

Thermodynamics of complex compounds of elements from the middle
of the fourth period of Mendeleev's system. Uch.zap.Kaz.un. 115
no.10:50-51 '55. (MLRA 10:5)

(Compounds, Complex)

YATSIMIRSKIY, K. B.

YATSIMIRSKIY, K.B.
USSR/Physical Chemistry - Atom

B-3

Abs Jour: Ref Zhur-Khimiya, No 5, 1957, 14336

Author : Yatsimirskiy K. B.

Inst : -

Title : Special characteristics of thirteen-electron ions

Orig Pub: Zh. neorgan. khimii, 1956, 1, No. 1, 96-99

Abstract: An examination is made of the relationship between the characteristics of bi- and trivalent ions of elements of the fourth period from Sc to Ga and the structure of the electron shells. It is shown that, in the series Ti^{2+} , V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Sc^{3+} , Ti^{3+} , V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} , Cu^{3+} , Ga^{3+d5} (thirteen pelectron), the ions Mn^{2+} , Fe^{3+} disturb the monotonous nature of the variation of certain characteristics: ionization potentials, oxidation potentials, ionic radii, heats of hydration, strength of compounds formed by these ions, vapor pressures of halide dissociation, crystalline structure of sulfides and

Card 1/2 Chemical Technol. Inst., Ivanovo.

USSR/Physical Chemistry - Atom

B-3

Abs Jour: Ref Zhur-Khimiya, No 5, 1957, 14336

Abstract: selenides of the type MX, rates of formation and decomposition of complex compounds. Disturbances of the monotony take place also in the case of Zn^{2+} and Ga^{3+} . All the disturbances are explained by the order in which the d-nuclei are filled by the electrons.

Card 2/2

YATSIMIRSKIY K.B.

USSR/Inorganic Chemistry - Complex Compounds, C

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 678

Author: Yatsimirskiy, K. B.

Institution: None

Title: Concerning Certain Functions Characteristic of Stepwise Complex Formation in Solutions

Original Periodical: Zh. neorgan. khimii, 1956, Vol 1, No 3, 412-421

Abstract: The basic functions which characterize stepwise complex formation in solutions are discussed: the "formation function" \bar{n} , the "degree of complex binding" ϕ (giving the ratio of the total concentration of the metal to the concentration of free metal ions), the "fraction of the given complex" α_m (giving the ratio of the concentration of a given complex (MA_m) to the sum of the concentration of all complexes and the free metal ions). The relationships between \bar{n} , ϕ , and α_m have been established, and the method for calculating any one of these functions from the others is indicated; \bar{n} , ϕ , and α_m can be calculated from the

Card 1/2

USSR/Inorganic Chemistry - Complex Compounds, C

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 678

Abstract: experimental data obtained during the study of stepwise complex formation by the solubility method, the distribution coefficient, ion exchange, by the potentiometric method, by the polarographic method, etc. Formulas are given relating the functions under discussion to experimentally measured values. From a series of values of \bar{n} , ϕ , and α_m it is possible to calculate the equilibrium constant for each step. Current methods for calculating the equilibrium constants are discussed and an improvement of a method previously proposed by the author is presented (Referat Zhur - Khimiya, 1954, 41064, 46234).

Card 2/2

YATSIMIRSKIY, K.B.

/ The kinetics and mechanism of the formation of urea 7

USSR/Inorganic Chemistry. Complex Compounds.

YATSIMIRSKIY, K.B.
Abs Jour : Referat. Zhurnal Khimiya, No 6, 1957, 18847

Author : K.B. Yatsimirskiy, I.I. Alekseyeva.

Inst :

Title : Study of Oxalate and Phosphate Complexes of Molybdenum by the Kinetic Method

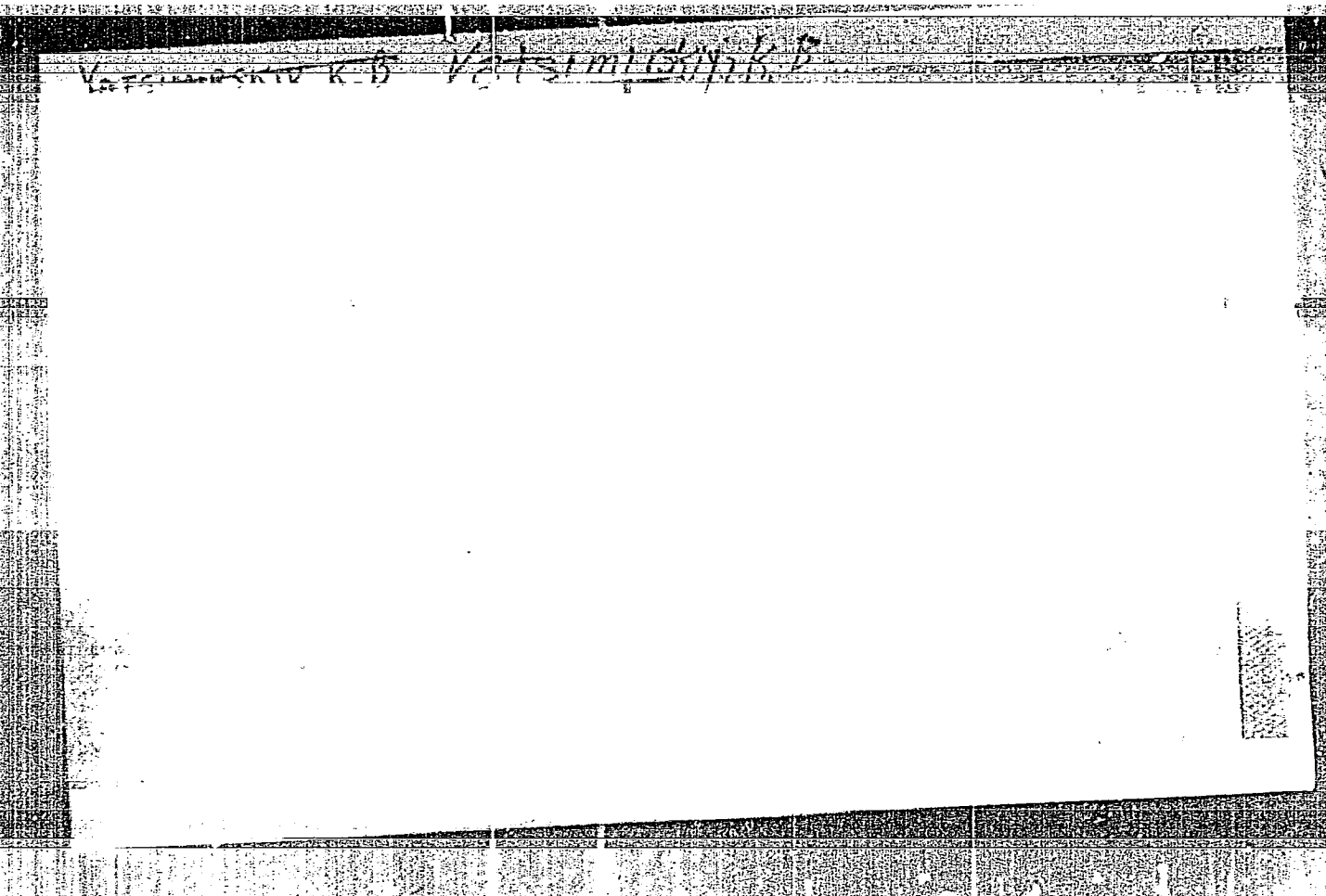
Orig Pub : Zh. Neorgan. Khimii, 1956, 1, No 5, 952-957

Abstract : The equilibrium in solutions of oxalate and phosphate complexes of Mo was studied on the basis of the measurement of the speed of the reaction of iodide oxidation by hydrogen peroxyde in an acid medium. This reaction is catalyzed by molybdic acid (I) (RZhKhim, 1956 78455). A decrease of the concentration of I in consequence of the formation of complexes causes a corresponding decrease of the reaction speed. Oxalic and phosphoric acids were used in excessive amounts as complex producing reagents. The concentration of the H^+ ions was 0.144 M. The kinetic study showed that I reacted with oxalic acid according to the equation: $H_2MoO_4 + H_2C_2O_4 = [MoO_2C_2O_4]$

Card 1/2

-26-

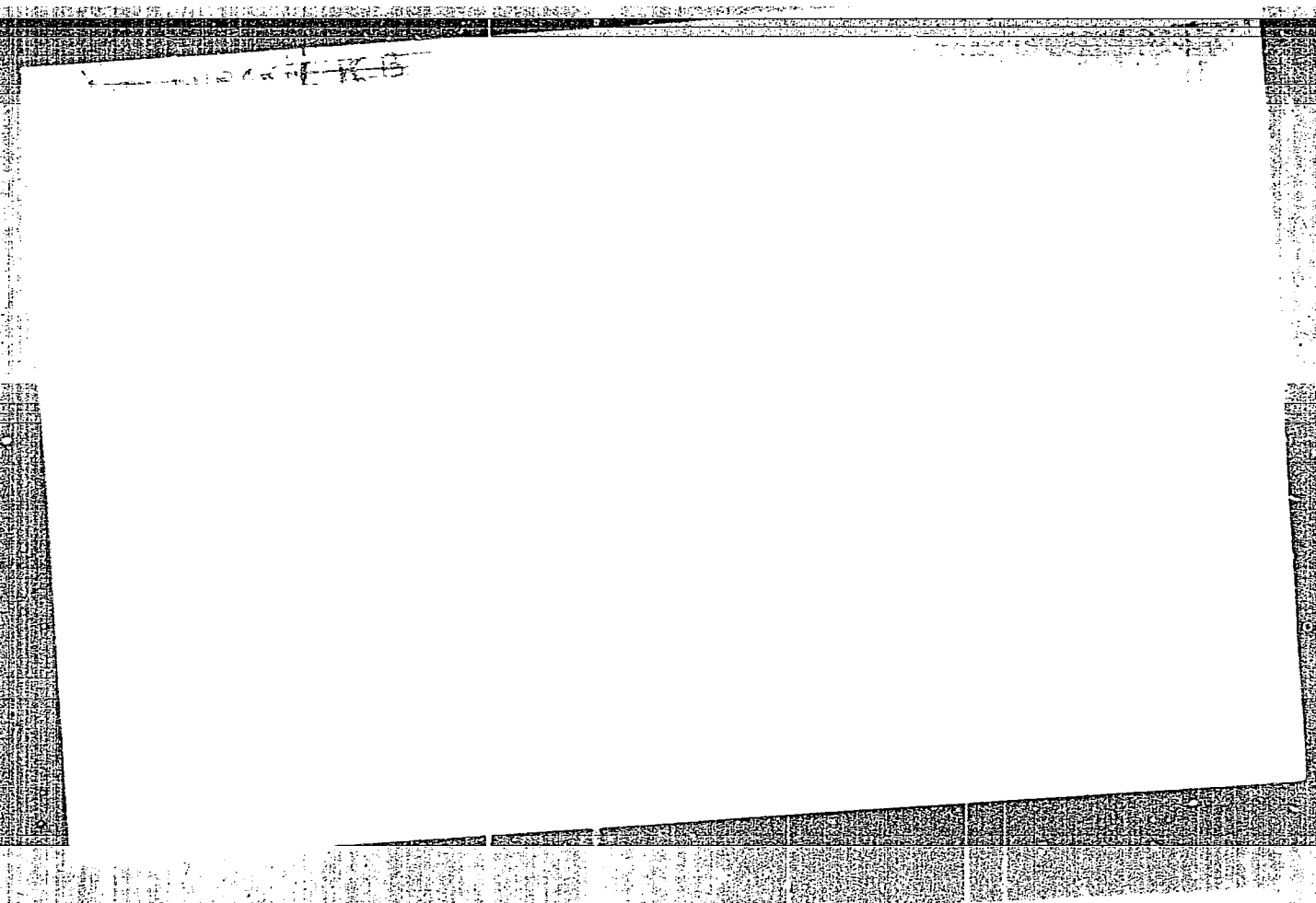
YATSIMIRSKIY, K.B.



YATSIMIRSKIY, K.B.

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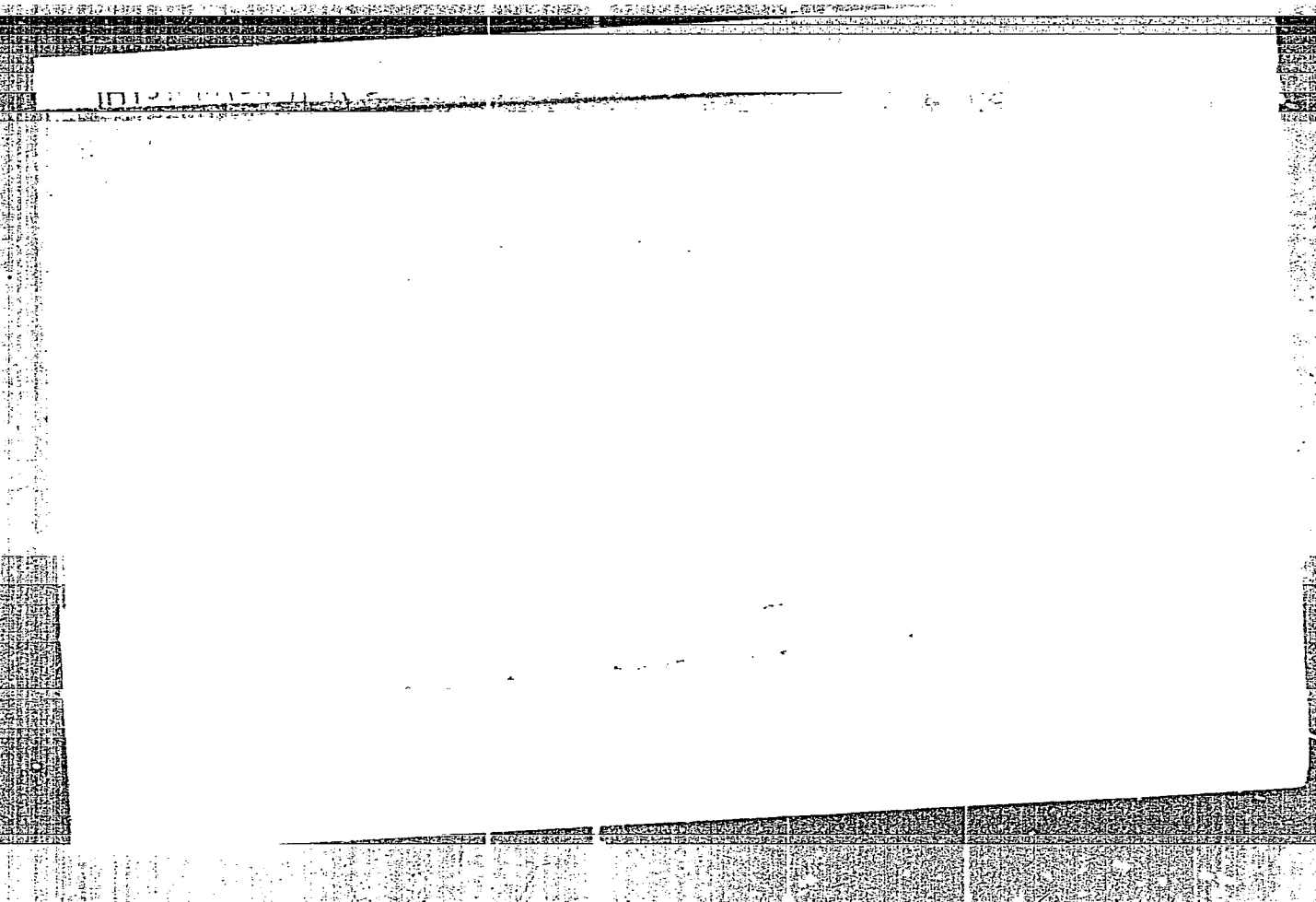
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7/1/06

APPROVED FOR RELEASE: 09/19/2001

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YATSIMIRSKIY, K.B.

✓ Kinetic methods of quantitative analysis. III. Deter-

2

5

made with 1.2×10^{-3} mole of 0.1937 g. per 100

Yatsimirskiy, K.B.

G-1

USSR/ Analytical Chemistry - General Questions

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11981

Author : Yatsimirskiy K.B., Astasheva A.A.
Title : Use of Solutions of Thiourea in Volumetric Analysis (Thiocarbamidometry)

Orig Pub : Zh. analit. khimii, 1956, 11, No 4, 442-446

Abstract : To 10-25 ml 0.025-0.2 M solution of thiourea (I) is added an indicator (15-20 drops of saturated solution of diphenylcarbazide (II) in alcohol or 10 drops of an analogous solution of α -nitroso- α -naphthol (III)), the mixture is diluted to 100-150 ml and titrated with a solution of $\text{Hg}(\text{NO}_3)_2$. On addition of II the solution acquires, at the transition point, a blue-violet coloration, while on addition of III it changes color from yellowish-green to yellowish-orange. Mean quadratic deviation is of 0.2-0.3% with II, and 0.1-0.2% with III. Back titration is also possible, although it is more appropriate, in the determination of Hg,

Card 1/2

G-1

USSR/ Analytical Chemistry - General Questions

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11981

to add a predetermined excess of I, and to titrate it thereafter with a solution of $\text{Hg}(\text{NO}_3)_2$. A pH value of 2 is optimal. Ag^+ , Cd^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Mg^{2+} , NH_4^+ ,

CH_3COO^- , SO_4^{2-} , NO_3^- and PO_4^{3-} do not interfere. I is used

also in the determination of Cd. To 20 ml of Cd-salt under study (0.01-0.05 M) are added 20 ml 0.25 M solution of I, 30-40 ml of saturated solution of picric acid, and the volume is brought up to 100 ml. After 15-20 minutes it is filtered through a dry filter and an aliquot portion (20 ml) is titrated with 0.25-0.05 M solution of $\text{Hg}(\text{NO}_3)_2$, using II as indicator. Mean quadratic deviation 0.23%. Lowest limit of determination $5 \cdot 10^{-4}\text{M}$. Determination is interfered with by Hg, Bi, Ag, Cu, Tl and large amounts of Pb. A 1000-fold excess of Zn does not decrease the accuracy, but delays substantially separation of precipitate.

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YATSIMIRSKIY, K. B.

USSR/Analytical Chemistry - General Questions, G-1

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61780

Author: Yatsimirskiy, K. B., Gruin, I. P., Kashirina, F. D.

Institution: None

Title: Determination of the pH of Alkaline Solutions by Means of Light Filters

Original
Periodical: Zavod laboratoriya, 1956, 22, No 3, 271-273

Abstract: For determination of pH of alkaline solutions by means of a set of indicators and a photometer with light filters (Referat Zhur - Khimiya, 1955, 21380) the following indicators are suitable: tropeolin 000, eosin, 2,4-nitrophenyl-azo-1-naphthol-4,8-disulfonic acid Na salt, alizarine red and tropeolin O. The pH interval is 7.5-13.4. Error of the method ~0.1. At very high values of pH the presence in the solution of ions carrying a large charge interferes.

Card 1/1

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YATSIURKIV K.B

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YATSIMIRSKIY, K. B.

USSR/Physical Chemistry - Crystals, B-5

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 195

Author: Kapustinskiy, A. F., and Yatsimirskiy, K. B.

Institution: None

Title: Lattice Energy of Salts Formed by Ions with 8-Electron Outer Shells

Original Periodical: Zh. obshst. khimii, 1956, Vol 26, No 4, 941-948

Abstract: In the formula for the calculation of the energy of the crystal lattice $U = 287.2 \frac{\sum n_K Z_K Z_A}{(r_K + r_A) \sqrt{1 - \rho/(r_K + r_A)}}$ (Kapustinskiy, Zh. obshst. khimii, 1943, Vol 13, 497) the value of the repulsion coefficient ρ depends on the sum of the ionic radii $\rho = 0.345 - 0.00870 (r_K + r_A)^2$. Using this empirical expression the following equation can be obtained: $U = 287.2 \times \frac{\sum n_K Z_K Z_A}{(r_K + r_A) \sqrt{1 - 0.345/(r_K + r_A) + 0.00870 \times (r_K + r_A)^2}}$, which gives values of U which agree with experimental values within 2% for salts of the type MX and MX_2 . The equation also gives satisfactory results for salts of the type MX_3 . Considerable deviations are observed in the calculation of U for salts in

Card 1/2

USSR/Physical Chemistry - Crystals, B-5

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 195

Abstract: which the cations are highly polarized. The value of U has been calculated for the oxides, sulfides, and selenides of the elements in groups I and II of Mendeleyev's periodic system. The values of the electron affinity of the atoms O, Se, and S have also been calculated.

Card 2/2

YATSIMIRSKIY, K. B.

Category: USSR

C

Abs Jour: RZh--Kh, No 3, 1957, 7802

Author : Yatsimirskiy, K. B.

Inst : Not given

Title : On the Question of Step-By-Step Complex Formation

Orig Pub: Zh. Obshch. Khimii, 1956, Vol 26, No 7, 2083-2084

Abstract: A review article. See RZhKhim, 1956, 19015.

Card : 1/1

-23-

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YATSIMIRSKIY, K. B.

USSR/Chemical - Physical chemistry

Card 1/1 Pub. 147 - 4/35

Authors : Yatsimirskiy, K. B., and Vasil'yev, V. P.

Title : Determination of instability constants of complexes by colorimetric measurement of the pH of the solution

Periodical : Zhur. fiz. khim. 30/1, 28-33, Jan 1956

Abstract : A new method was developed for colorimetric determination of pH in highly dilute sodium pyrophosphate solutions. The method was tested on several series solutions containing calcium nitrate and sodium pyrophosphate and was found to be perfectly suitable for such type of measurements. The instability constant of a calcium pyrophosphate complex was computed on the basis of results obtained by this new method. Five references: 3 USSR and 2 USA (1928-1954). Tables; graph.

Institution : Chemicotechnological Institute, Ivanovo

Submitted : March 14, 1955

YATSIMIRSKIY, K.B.

Category: USSR / Physical Chemistry
Thermodynamics. Thermochemistry. Equilibrium. Physico-chemical analysis. Phase transitions.

B-8

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 29880.

Author : Yatsimirskiy K. B., Vasil'yev V. P.

Inst : not given

Title : Thermochemistry of Pyrophosphate Complexes in Solution

Orig Pub: Zh. fiz. khimii, 1956, 30, No 4, 901-911

Abstract: Determination of the heat of mixing values of solutions of nitrates of Ni, Cu, Zn and Pb with solutions of sodium pyrophosphate of different concentration, and also of the heat of dilution of the above-stated salts. The determinations were carried out in the previously described calorimeter (RZhKhim, 1955, 32011) which has been improved by the authors. From changes in heat of mixing value, with change in concentration of sodium pyrophosphate solution, the stepwise constant of instability of $\text{Ni}(\text{P}_2\text{O}_7)^{4-}$ was calculated. Enthalpy change (ΔH) in the reaction $\text{Ni}^{2+} \text{aq} + \text{P}_2\text{O}_7^{4-} \text{aq} = \text{NiP}_2\text{O}_7^{2-} \text{aq}$ (1) is 4.21 ± 0.04 kcal.

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Card : 1/2

Category: USSR / Physical Chemistry.
Thermodynamics. Thermochemistry. Equilibrium. Physico-
chemical analysis. Phase transitions.

B-8

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 29880

Author : Yatsimirskiy K. B., Vasil'yev V. P.
Inst : not given

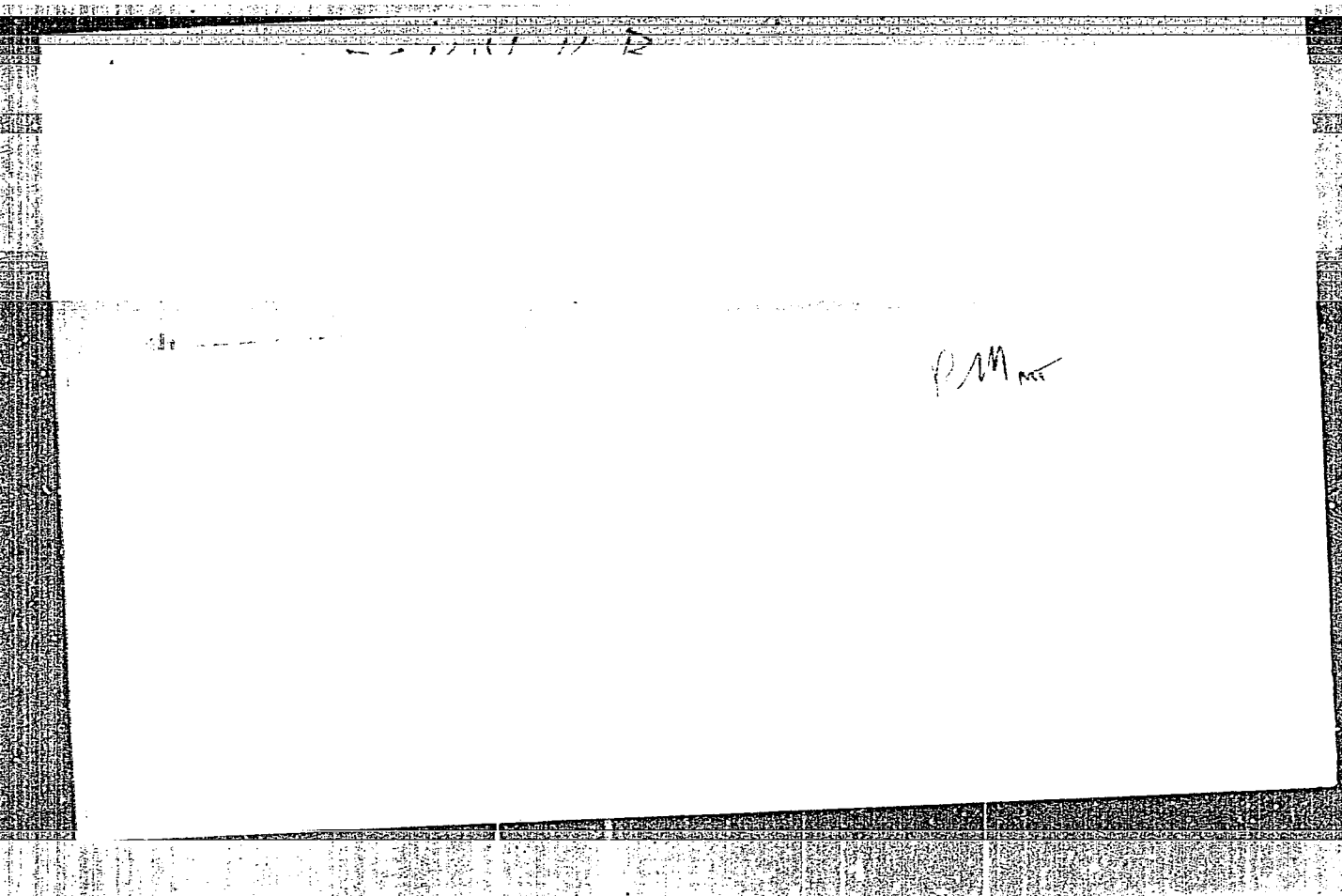
In reactions of the type $M^{2+}aq + 2P.O_7^{2-}aq = M(P.O_7)_2^{2-}aq$ (2)
the ΔH for Ni, Cu, Zn and Pb is, respectively, 2.00 ± 0.02 ;
 -0.67 ± 0.07 ; 2.64 ± 0.05 and -1.01 ± 0.11 . Values of standard
heat of formation have been calculated for the complex ions $NiP.O_7$
and $M(P.O_7)_2^{2-}$ (M -- Ni, Cu, Zn and Pb). For reactions of type (2)
change of isobaric thermodynamic potential and entropy have been
calculated. Entropy change in these reactions satisfies the equa-
tion: $\Delta S = 0.1 L_{H_2O} + \text{const}$ (3), where L_{H_2O} is heat of hydration of
 M^{2+} ion. Equation (3) is utilized to calculate the instability
constant of $Pb(P.O_7)_2^{2-}$ ion, together with the thermochemical
data.

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Card : 2/2

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APPROVED FOR RELEASE: 09/19/2001

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DRAKIN, S. I. and YATSIMIRSKIY, K. B. (Ivanovo)

"The Entropy of Ion-Solvation,"

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AUTHORS:

Yatsimirskiy, K.B. and Tetyushkina, V.D.

TITLE:

Influence of Ionic Force on the Instability Constants of Halogen and Pseudo-Halogen Complex Compounds. (O Vliyanii Ionnoy Sily na Konstanty Nestoykosti Galogenidnykh i Pseudogalogenidnykh Kompleksnykh Soedineniy).

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ABSTRACT:

The range of applicability of empirical equations such as that of Davies (9) and the concepts of ionic force is still undecided. The research described is a contribution on this problem and involved the optical investigation of the thiocyanate complex of iron in the visible part of the spectrum. Relatively low concentrations of ferric nitrate (0.004974 mol/litre) and potassium thiocyanate (0.0004977 mol/litre) were used, enabling a wide range of ionic forces, from 0.25 to 3.5, to be covered. The bromide complex was also studied. Potassium, magnesium and aluminium nitrates were used to produce definite ionic forces.

Determinations were thus made of the instability constants and of the influence on complex-formation equilibria in the systems Fe^{3+} - CNS- electrolyte and Fe^{3+} - Br- electrolyte. It was shown that the ionic-force concept is valid up to forces of the order of 1.5 if the accuracy limit for the instability-constant indices of the complexes is taken as ± 0.1 ;

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